PRACTICAL MICROSCOPICAL METALLOGRAPHY

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PREFACE

THE preparation of a third edition of this book has afforded an opportunity for revision and enlargement. Various sections dealing with the structure and constitution of alloys have been rewritten and expanded. Some additions have been made to the chapter dealing with the microscope and method of microscopical examination, and also to the practical notes on particular materials. Reference has been made to the latest developments of objectives and illuminants for microscopy; and among the additional illustrations are photomicrographs taken with the equipment described. Other new photographs illustrate structures observed in the alloys of copper, of zinc and of lead.

In its aim and character the book is essentially concerned with the methods and results of the examination of metals and alloys by the aid of the microscope. Our intention has been to provide, within a small compass, a set of typical photomicrographs, suitably annotated, and accompanied by a concise account of the results of metallographic researches and other investigations, in so far as they afford an interpretation of the structures observed in commercial materials and illustrated in the photomicrographs.

We have kept in mind the needs both of metallurgical students and of students of engineering who study metallography as a part of their engineering course. Metallurgists and engineers are on common ground in considering the strength and properties of engineering materials. In this book, therefore, the structures of metals and alloys of industrial importance are considered in detail in the light of their

constitution, but with special reference to their mechanical properties and practical utility. A full description is also given of the technique of microscopical examination and of photomicrography; and methods of overcoming practical difficulties which may be encountered are indicated. It is thus hoped that the book may also be of value to independent workers, practising engineers and other users of metals who desire to avail themselves of this method of examination.

All the photomicrographs in this book were taken at University College, Cardiff, or at the Research Department, Woolwich. We wish to express our thanks to Prof. A. A. Read at whose suggestion the book first took shape; to Dr. W. R. D. Jones for supplying photomicrographs to illustrate the structure of the copper–magnesium alloys; and to the Director of Artillery for permission to make use of a number of photomicrographs taken by our colleagues and ourselves in the course of our duties at Woolwich.

R. H. G.
H. W.

October, 1939.

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In this new impression only a few small amendments have been introduced and one of the illustrations (Fig. 311) has been replaced by a photomicrograph for which the authors are indebted to Mr. K. J. B. Wolfe, B.Sc.

R. H. G.
H. W.

February, 1941.

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CHAPTER I

INTRODUCTION

THE term Metallography is not confined merely to the visual or microscopical examination of metals, but now comprises all methods employed in the study of the constitution and internal structure of metals and their alloys, and the influence of structure and constitution on the physical and mechanical properties.

Although there are scattered records of the microscopical examination of metals by several earlier investigators, the work of Sorby in the middle of the nineteenth century marked the first systematic attempt to discover by the aid of the microscope the distinguishing structural characteristics of different samples of iron and steel. Sorby in 1856 established the practice of microscopical examination of rock sections and founded the science of petrography: and by an extension of the same idea and modification of the technique he began, before 1864, to turn his attention to metallurgical products. In 1886 he announced the discovery of the "pearly constituent" as a characteristic feature of carbon steels. Microscopical examination of metals was taken up independently by Martens (1878) and Osmond (1880), Sorby's work was continued later by Arnold, while Stead, Roberts-Austen, Howe, Charpy, Heycock and Neville and others were among the pioneers of metallographical research.

At the suggestion of Howe the various constituents of steel were defined by mineralogical names to facilitate reference. Thus crystals of pure iron were called "ferrite," carbide of

iron "cementite," and Sorby's "pearly constituent" became known as "pearlite." Later, personal names were pressed into service for constituents or characteristic structures, *e.g.* sorbite, austenite, martensite, etc. Fortunately these complexities of terminology have been avoided in the more recently developed metallography of the non-ferrous alloys.

The constituents of the microstructure of a metal or alloy are formed during solidification from the liquid or during transformations which subsequently take place in the solid metal. The appearance of the structure alone will not give full information regarding its origin or the relation of one constituent to another.

Hence the microscope was supplemented at an early date by other instruments of research, notably the pyrometer, and it was mainly by the aid of these two that the foundation of the new science of metallography was laid. By means of the thermo-couple and the electrical resistance pyrometer, accurate temperature measurements at high temperatures became possible, and the freezing points and other thermal changes in metals or alloys were observed. The results of thermal and microscopical examination in conjunction with chemical analysis have been condensed into "equilibrium diagrams," the construction and interpretation of which will be referred to in more detail later. Of recent years, crystal analysis by X-rays has furnished a most effective method of investigating the constitution of alloys, by providing a knowledge of their internal structure and the changes it undergoes with change of composition, both at atmospheric and at high temperatures. Specific volume, magnetic properties, electrical resistance, thermo-electric properties and electromotive force have all been used to confirm and extend the results of thermal and microscopical examination. In addition to the essential value of chemical analysis in defining the ultimate composition of the material as a whole, separation of individual constituents has been accomplished by chemical methods in some cases.

Mechanical properties, such as hardness, tenacity and ductility, are continually being correlated with microstructure, while the numerous defects to which commercial metals and alloys are liable are almost invariably associated with abnormalities of structure. It is to illustrate this aspect of the subject that the following pages are mainly directed: the matter treated is narrowed down to that which may be included in the term "microscopical metallography," *i.e.* the examination of the structure of metals and alloys, by the aid of the microscope. Without the evidence of the subsidiary methods of examination referred to above, the micrography of metals would be little more than a collection and attempted classification of the structures characteristic of particular metals or alloys, but subject to enormous and inexplicable variations. In order to explain and systematise the data obtained by microscopical examination, it will therefore be necessary to introduce the results of other methods of metallographic investigation, though for detailed information regarding these, the reader is referred to books dealing more generally with the subject of Metallography.

Constitutional Diagrams.—The temperatures at which changes in the constitution of alloys occur, under conditions as nearly approaching true equilibrium as can be attained, are determined experimentally and recorded in a simple graphical manner. The horizontal axis represents composition, the vertical axis temperature. The diagram will contain a curve passing through all the points which represent temperatures at which alloys of different compositions begin to freeze, or at which melting is complete. This is known as the liquidus. Below this will be a curve joining up all points which represent the temperature at which solidification is just complete on cooling, or at which melting just begins on heating. This is the solidus. The physically distinct portions of the alloy system which undergo these changes are known as phases. Thus, the homogeneous liquid solution of one metal in another is a phase, and if the metals are completely miscible in the

liquid state, there is only one liquid phase. The solid which is formed on solidification is another phase, and if in the solid alloy different kinds of solid substance (which, however, must be chemically and physically homogeneous throughout) are microscopically visible alongside of one another, more than one phase is present, though possibly not more than one phase will remain when equilibrium is attained by annealing. If alloys undergo changes in the solid state, the temperatures at which they occur are recorded as points in the constitutional diagram: the same type of change occurring over a range of composition is revealed as a line joining up individual points.

When all such changes have been inserted, the diagram becomes a complete chart of the various conditions assumed at different temperatures by an alloy of any composition within the system dealt with. A simple check on the accuracy of the diagram is afforded by the physico-chemical principle known as the Phase rule. This tells nothing about the character or properties of the phases, but merely defines how many different phases may exist together in a system in true equilibrium under varying conditions of composition, temperature and (if a vapour is concerned) pressure. By true equilibrium is meant a state which shows a continuous change with change of conditions, *e.g.* temperature, but which is always the same no matter in what direction it is approached, *e.g.* by heating up or by cooling down. There are many alloys which appear to be, and are practically, in a perfectly stable state, since they have existed unchanged for a period of centuries, but yet they are not in true equilibrium. If they are heated slightly and then slowly cooled, they do not regain their original condition, but undergo a change which is always in the nature of closer approach to true equilibrium.

The accurately determined constitutional diagram represents the condition of true equilibrium between the constituents at any given temperature: but it is important for those who, for practical purposes, wish to interpret microstructures in the light of the equilibrium diagrams, no less than for those

engaged in their actual determination, to recognise how the microscopical method is employed in their construction. Its use depends on the assumption that an alloy can be brought into its condition of equilibrium at any given temperature and that its structure in this condition can be retained by quenching. The first assumption is generally correct, though it is now recognised that, except at high temperatures, equilibrium is very slowly attained by annealing. Thus whereas annealing for a few hours may be employed in practice, annealing for days or even months may have been necessary in the investigation of equilibrium conditions. The second assumption is by no means universally true, even for very rapid quenching carried out on small pieces; but the significance of the structure is usually not misleading to the trained investigator, since its appearance, in conjunction with information given by cooling curves, leaves no doubt that the change has occurred or has started to occur. In practice, however, complete retention by quenching of a condition stable at high temperatures is not often possible.

Commercial alloys are rarely in a condition of true equilibrium, but this does not detract from the practical value of the constitutional diagram. In fact, no diagram which is intended to become more and more accurate in detail with increasing knowledge could ever be framed to express conditions other than those of true equilibrium. A comparison of the structure of a commercial alloy with that required by the diagram will indicate the possibility of change, and the direction in which the change will tend to occur if a high-temperature treatment is applied to the alloy. The exact limits of composition beyond which deleterious constituents are bound to occur or within which their separation may be suppressed by heat treatment are shown by the diagram, and a rational basis for the choice of correct temperatures in heat treatment is provided.

CHAPTER II

PREPARATION OF SPECIMENS FOR MICRO-EXAMINATION

Sampling.—For convenience in manipulation it is advisable to keep the size of the specimens for microscopical examination within the limits of $\frac{1}{4}$ to 1 inch square or diameter, whenever possible. Very small or very large specimens are more difficult to polish, the former because of a tendency to rounding of the edges, the latter on account of the difficulty of removing all scratches. The specimen is easier to hold if its thickness is less than the linear dimensions of the polished face: $\frac{3}{16}$ to $\frac{3}{8}$ inch are convenient thicknesses. For very thin specimens special methods of mounting have to be employed.

Specimens should be selected from various positions which will suggest themselves according to the character of the material and the object of the examination. Thus, from a rolled rod both transverse and longitudinal sections should be examined, from a casting the whole cross section should be explored to observe differences from inside to outside, and so on. In some cases it may be necessary to make a preliminary examination of very large pieces, but after this has been carried out at low magnifications, they should be cut up for more detailed examination. In investigating material which has failed in use, large numbers of sections are sometimes required. Examination in the neighbourhood of the fracture should be supplemented by a general examination of the material for the purpose of revealing any lack of uniformity of composition and treatment. It should be remembered that in some cases, after annealing, the material near the outer skin may be altered; thus steel may be decarburised, or a brass may lose some of its zinc.

The specimens should, when possible, be cut out by hack saw, the blade of which should be lubricated by applying soap solution at intervals with a brush. For large material, preliminary cutting by other means—lathe, shaping machine or band saw—is required. Violent mechanical action must be avoided as likely to cause distortion of the material (see Fig. 6), and no method which involves heating of the material (such as oxy-acetylene cutting) should be used. Even a slight rise of temperature is sufficient to cause an alteration of structure in hardened steels. Hard steel specimens may have to be cut or shaped by an abrasive wheel. As low a speed as possible should be used together with a copious flow of water. With a high speed of grinding, intense heat may be developed locally, causing alteration of structure with formation of a fine network of cracks produced by rapid heating and chilling.

Preparation of Specimens of Steel.—A specimen of convenient size having been cut, a level surface should be produced by shaping or filing. From the beginning care should be taken to minimise the depth of the flow and distortion which occurs below the worked surface. Deep file marks or a heavy saw-cut may not only completely alter the structure of the underlying metal, but may conceal the existence of porosity and cracks.

After the surface has been levelled by rubbing it on a fine file or by grinding wet in a surface-grinding machine or on a slow-running grindstone, the corners and edges of the specimen, which are apt to tear paper and cloth at subsequent stages of polishing, should be rounded off. If for any purpose, such as the examination of cracks, decarburisation, etc., an edge of the specimen must be preserved for examination the other edges and corners should be rounded off.

The specimen is then ground on successively finer grades of emery paper. Each sheet, when in use, is laid on plate glass about $\frac{1}{4}$ inch thick and the specimen is held face downwards on it and given a steady to-and-fro motion towards and away from the operator, until an even system of parallel

scratches is produced. At each transfer to a finer grade of paper, the specimen itself, the glass plate and the surrounding bench should be dusted to remove emery particles, and grinding continued in a direction at right angles to the previous series of scratches until these are entirely replaced by a new system of finer scratches at right angles to the first.

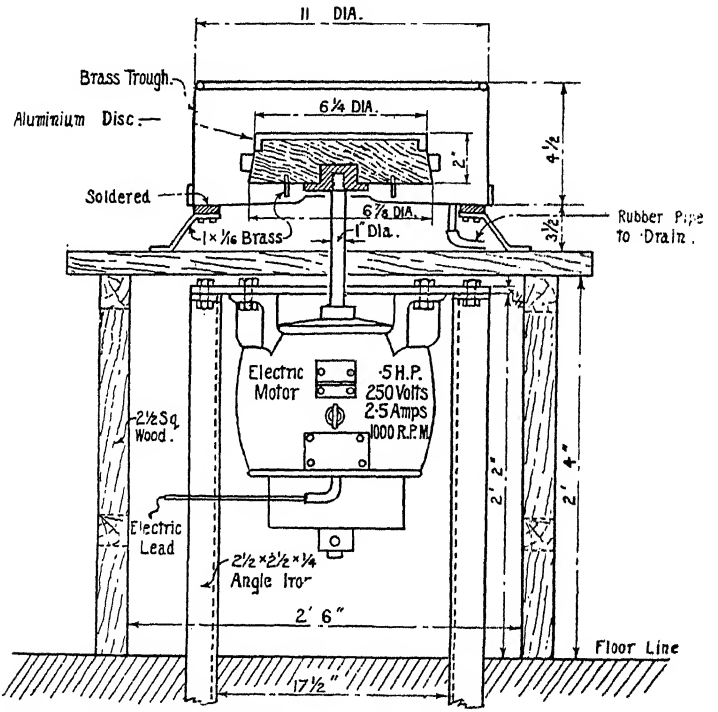


FIG. 1.—Arrangement of Motor and Polishing Block (not to scale). An adjustable external resistance is used to obtain slower speeds down to 300 revs. per min.

For the early stages of this process, emery cloths or the coarser papers of any make will probably prove to be quite suitable. The primary object is the removal of distorted and flowed metal. Whenever material is to be examined for defects, such as fine cracks, porosity or inclusions, grinding on each of the coarser emery papers should be continued well beyond the stage at which the previous scratches become obliterated. Minute defects in the metal will not be exposed

unless the distorted material underlying the original cut surface has all been removed.

For the further stages of grinding, the special French emery papers (*e.g.* Fortin's or Hubert's Qualité supérieure) will be required. A suitable selection would be the M, F and 0, 00 and 000 grades. It is essential that transfer from one paper to the next should not be made until all scratches are in the same direction (see Fig. 7), and that the pressure exerted should not be so great as to raise the temperature of the surface of the specimen appreciably. Prolonged grinding with these, as with the coarser papers, may sometimes be advisable. Inclusions present in steel are apt to be torn from their cavities by coarse emery particles. Graphite in cast iron is specially subject to damage in this way. Continued grinding on the finer papers may be necessary to reveal the enclosed material intact and unbroken.

After coming from the 000 emery paper, the specimen is ready for finishing. It is rinsed in water and then held against a rapidly rotating disc covered with a suitable pad impregnated with a polishing powder (Fig. 1).

A suitable polishing medium for general use is alumina, sold under the trade name of "diamantine," but easily prepared in any laboratory in the following manner:—Pure ammonium alum is heated in a porcelain or silica dish over a Bunsen burner to decompose it and drive off the water of crystallisation. It is then strongly heated in a muffle at 1000° C. for 4 or 5 hours, any crust formed being broken down at intervals. There should be a current of air in the muffle to remove acid fumes. The product, after cooling, crumbles to an impalpable powder, which is bottled and without any further treatment constitutes a satisfactory polishing medium.

Magnesium oxide, in the form sold as "heavy calcined magnesia" without further preparation, is a satisfactory polishing powder when used with a copious supply of water. If the water supply contains much dissolved carbonate, dis-

tilled water should be used. The pad should always be removed and washed in dilute hydrochloric acid to free it from magnesia after use, otherwise hard particles of magnesium carbonate are formed.

Although it is not strong and wears out quickly, the cloth known as selvyt makes an excellent pad, and when used wet (as it almost invariably is) is superior to wash-leather. Serge suiting cloth is a very satisfactory material for polishing iron and steel specimens; it enables a suitable finish to be obtained more quickly than with selvyt, but it is too hard for use with the softer metals. Cuttings may be obtained cheaply by arrangement with a firm of tailors. The cloth or selvyt is stretched on a disc, which may be of hard wood or wood covered with aluminium, and is held by means of a ring: it is flooded with water and, after the water has soaked in, the alumina is applied and gently rubbed round with the finger. The disc is rotated and fed with water while the specimen is held against the surface. To eliminate scratches and ensure an even polishing effect the specimen should be slowly moved in the reverse direction to the rotation of the disc.

A plentiful supply of water and of polishing medium should be used. It is indispensable to keep the specimen wet; if dry, alumina becomes embedded in the surface and is not removed by subsequent polishing. When inspection shows that the surface is free from scratches the specimen is well washed under the tap and carefully dried on a soft cloth. It may be examined with a small lens or put under the microscope to judge the success or otherwise of the polishing operation. One or two minutes on the polishing wheel should be sufficient for a specimen $\frac{1}{2}$ or $\frac{3}{4}$ inch square. If only a few faint scratches are visible at a magnification of about 50 the specimen is suitable for all ordinary purposes of examination. If many scratches persist a return should be made to a fresh sheet of the final grade of emery paper.

Alternative Methods of Polishing.—There are or have been in use a large number of methods of preparation of sections for microscopical examination. For example, a method in common use is to carry out all the polishing on rotating blocks, fitted with emery paper of necessary fineness, and finally on a pad fed with water and alumina. The main objection to this method is that heating and alteration of the surface are almost impossible to avoid. It has the merit of being rapidly carried out and is useful for many commercial purposes.

Rouge was frequently used, and is still sometimes employed as a polishing medium. As an abrasive it is inferior to alumina and magnesia. It takes longer to eliminate the scratches made by emery paper, and the quality of the surface suffers even when the rouge is used wet on kid-skin or wash-leather. The use of dry rouge for finishing cannot be too strongly condemned. The adherence of dry rouge to the surface during polishing is even more pronounced than that of alumina mentioned above, the surface of steel eventually becoming opalescent.

This fact illustrates a condition which accompanies polishing and is of very great importance in connection with the polishing of soft metals. The mechanical action of polishing produces on the surface of a metal a thin layer the structure of which is different from that of the interior. This amorphous layer shows the properties of a viscous liquid, for example, in its tendency to flow under the influence of the forces exerted in polishing. The flow of metal of this amorphous layer is most marked when dry burnishing powders are used, and least marked when wet abrasive powders are employed. The presence of a thin amorphous layer is not detrimental to micrographic examination, since it is removed by etching; but "buffing," or the production of a "forced polish," is fatal, because it does not permanently eliminate, but merely smoothes over and covers the scratches (Fig. 8). The first action of the etching agent in dissolving away the surface

layer will therefore be to reveal the original scratches in as great a number as ever (Fig. 9).

Preparation of Specimens of Soft Metals. — The liability to form an altered amorphous layer necessitates that very special precautions shall be taken with soft materials. In the case of copper or soft brass, polishing is carried out under slight pressure on a slow-running disc fed with alumina and water in the usual way. The final polishing is often carried out by means of metal polish (liquid or paste) on selvyt or on chamois leather. Fresh pieces of chamois leather should be frequently used, as they harden when the polish dries on them. It is essential, after polishing with many such media, to wash the specimen in warm caustic soda solution, to remove all grease before etching.

In the case of aluminium and its alloys, the preliminary preparation differs only in the necessity for exercising greater care. Thus the emery papers used should be waxed or soaked in paraffin to prevent embedding of particles of emery on the surface. For final polishing, commercial magnesia powder on a soft woollen cloth has been found satisfactory if the precautions already described are observed in its use.

In preparing specimens of very soft metals the final polishing is done by hand with liquid metal polish on selvyt stretched on a board. This leaves a film of grease, which is removed by rubbing on selvyt wetted with benzene or acetone.

A method of preparation of microsections of lead and other soft metals, which has been developed in America and may become more widely used in the future, involves the use of a heavy and massive microtome. If the knife of this instrument is designed and ground correctly, specimens may be prepared by its use without distortion or dragging of the surface, and a very short final polish is all that is necessary before examination. Plane surfaces, suitable for examination, of metals and alloys with a low melting point can often be obtained by casting the metal on to a smooth or polished surface such as plate glass, mica or polished steel.

Electrolytic Polishing.—To overcome the difficulties experienced in polishing soft metals by the ordinary methods, Jacquet has suggested the use of electrolytic polishing and has worked out conditions suitable for the polishing of copper and its alloys, aluminium and other metals.* A copper specimen finished on 000 emery paper and degreased is made the anode in a phosphoric acid solution (530 grammes of pyrophosphoric acid per litre) at a current density of about 15 amperes per square decimetre for 10 or 15 minutes. For aluminium, a solution of acetic anhydride and perchloric acid is used, and a current density of 3 to 5 amperes per square decimetre for a similar time. The solution must be carefully made by pouring very slowly 785 c.c. of acetic anhydride into 215 c.c. of an aqueous solution of perchloric acid (density 1·480), the liquid being kept cool continuously. The treatment must be sufficiently prolonged to remove the altered layer produced by previous cutting or grinding. After electrolytic polishing the specimen is washed and etched in the usual way or it may be etched electrolytically in the solutions used for polishing, but at a lower current density (about 1 ampere per square decimetre).

The process may be applied to specimens of all sizes, including sections for macro-examination. Its use has been extended to the polishing of iron and steel. A specimen prepared on 000 emery paper requires about 5 minutes at 4 to 6 amperes per square decimetre in a solution similar to that used for aluminium. The attack of etching reagents is said to be much more active and non-metallic inclusions and flaws to suffer less risk of damage than on surfaces produced by mechanical polishing.

Development of the Structure.—The dry specimen after polishing should always be examined unetched. Inclusions, flaws and other defects are immediately observable, the form of such constituents as graphite in pig iron is most

* Abstracts of Jacquet's work appear in *The Metallurgist*, Aug. 1936, p. 150; April 1938, p. 116, and June 1939, p. 39.

readily examined, or coloured constituents which occur in some non-ferrous alloys observed. Occasionally the harder constituents stand out in relief, and their form is distinctly visible. Dry polishing assists in throwing constituents into relief, but its indications must be accepted cautiously on account of the possibility, mentioned above, of alteration to the surface during polishing. Even after careful polishing at a slow speed the amorphous film may flow over and obscure very fine cracks, and if these are to be recognised with certainty the specimen should be etched to remove the altered ayer and then lightly repolished by hand on selvyt moistened with liquid metal polish.

The usual method of revealing the structure of polished specimens is by etching. Etching reagents act by the gradual solution of the metal from the surface downward, the rate of solution being modified by local peculiarities of the metal. In a pure metal containing only one constituent, etching generally proceeds slowly, the grain boundaries are rather more quickly attacked than the interior of the grains, and a system of polyhedral grains is gradually revealed. In an alloy containing two or more constituents, if one constituent is electro-positive to the other, electro-chemical action will take place, in which case the rate of solution of one constituent may be negligible while another is rapidly corroded. In these circumstances etching takes place much more quickly. Work has been done correlating the speed of attack with the ionising power and other properties of the solvent. By the use of a suitable solvent (*e.g.* amyl alcohol) very slow attack may be obtained. For practical purposes a reagent is required which produces the desired effect in not less than 10 seconds or more than about 2 minutes. The uniformity of etching obtained with alcoholic solutions is usually greater than with aqueous solutions, and staining is less common.

It is impossible to lay down general rules for the time of etching. The degree of etching which gives the best results varies according to the magnification at which the specimen is

to be examined. For high magnifications the etching should not be so prolonged as for low magnifications, since differences of level are produced which render focussing difficult.

Irregular etching is liable to occur when the metal shows any degree of passivity towards the reagent, or when a water solution is used if the slightest film of grease is present. It may best be overcome by rubbing the specimen for a few seconds on a pad soaked with the etching reagent, diluted if necessary, until it is seen that an attack has commenced; it may then be transferred to a dish containing the normal etching solution, and the attack will continue uniformly. No noticeable relief or polish attack is given by the short preliminary rubbing.

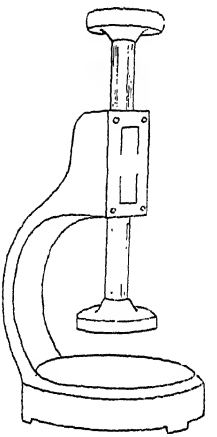


FIG. 2.—Device for levelling Metal Specimens mounted in Plasticine.

The specimen after etching should be thoroughly washed in a stream of running water, and subsequently in alcohol or acetone. The sides of the specimen are then wiped, but the surface is allowed to dry untouched. A current of warm air from a small electric hair-dryer is useful for drying specimens rapidly.

The specimen is embedded in plasticine attached to a

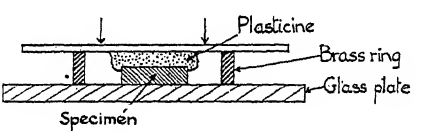


FIG. 3.—Method of levelling Metal Specimens mounted in Plasticine, by means of a Brass Ring.

glass slip, and the surface levelled by means of a device such as that shown in Fig. 2. In an equally satisfactory alternative method of mounting, the specimen is placed face downwards on a glass surface, surrounded by an accurately parallel brass ring, and mounted on a glass slip in plasticine in the manner indicated in Fig. 3. If the strip is then placed on the micro-

scope stage the specimen adhering to it presents a parallel surface and no further levelling is required.

Methods of dealing with Thin Strip, Sheet or Wire.—Specimens of thin strip or sheet may be polished on the surface by attaching them to another metal or to wood by means of sealing-wax or glue. For examination of cross sections the strip may be inserted in a slot cut in a block of soft metal which is then gently squeezed on the specimen to grip it (Fig. 4). The whole block is then shaped down and ground, and the composite surface, including the strip or wire, polished and subsequently etched in the usual manner. The etching of steel, brass, copper or aluminium sheet is satisfactorily accomplished in this way, using a holder made of similar

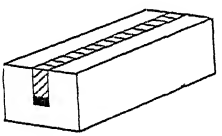


FIG. 4.—Method of mounting Strip or Wire in a Metal Block.

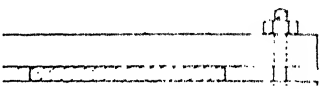


FIG. 5.—Clamp for holding Strip or Wire. (*N.P.L.*)

metal. Any difficulty experienced through staining produced by traces of the etching medium oozing out at the junction of the strip and holder may generally be avoided by immersion of the specimen in a bath of acetone for 10 minutes or more before it is dried, or by final washing with ether, which dries so rapidly that the capillary forces which cause creeping of the reagent from the cavities have no opportunity of coming into play.

As an alternative method of mounting, a clamp such as that shown in Fig. 5 may be used, and the composite face ground and polished as before. The specimen is removed for etching and returned to the holder for examination.

Wire may be mounted by inserting it vertically in a cylindrical hole punched with a pencil in plasticine, then casting round the specimen a fusible alloy such as Wood's metal (Bi 4 : Pb 2 : Sn 1 : Cd 1, m. p. 70° C.). A composite sec-

tion through specimen and white metal is then cut, polished and etched in the usual way.

A more satisfactory method of mounting is in bakelite or some other synthetic resin which when set, is not attacked by alcohol or other solvents used in the etching process. Presses specially made for this purpose are now available. The specimen, cleaned and freed from grease, is surrounded by the mounting material in powder form and subjected to pressure at a temperature of 100° to 150° C. It thus becomes embedded in a hard mass with very close contact at all points. After the initial heating of the press, samples can be mounted in ten minutes or less.

Specimens too large for a press of this type, or those with structures which might be affected at temperatures above 100° C., may be mounted in fluid bakelite (Bakelite cement N.P.A.) contained in a suitable mould and heated at 55° to 60° C. for a period up to 48 hours in a small thermostatically controlled oven. It has not been found necessary to extract the solvent from this material by a vacuum pump, but on the other hand any attempt to hasten this process by using a higher temperature will probably produce a soft spongy mass instead of a hard setting.

Protection of the Edges of a Specimen in Polishing.—In certain cases, *e.g.* the examination of surface hardening, case hardening, decarburisation, plated goods, study of fractures, etc., it is necessary to examine the structure right up to the edge of the specimen. In the case of specimens with a hardened skin this can be done by exercising care in polishing, but with other material the edges always become slightly rounded. To avoid this effect the specimen may be mounted in fusible metal in a manner similar to that described above. This, however, may not preserve the minor irregularities of a surface, and is unsuitable for such materials as tinplate. Copper, deposited first with a weak current in a cyanide bath and then with a heavier current in an acid sulphate bath, affords a suitable protection in such cases.

Alternative Methods of Revealing the Structure.

Polishing in Relief.—This effect may be produced in specimens containing a hard constituent if polishing of the surface, carried out in the ordinary way, is continued on a soft parchment or cloth pad which may be impregnated with a little of the finest rouge or calcium sulphate and washed with water at intervals.

Polish Attack is carried out by very lightly polishing on a parchment pad moistened with a suitable etching agent. For steels this may be a 2 per cent. solution of ammonium nitrate in water. For copper and brass a 5 per cent. solution of 0·880 ammonia in water is used. By this method staining is avoided. There is a danger of over-emphasising grain boundaries, but with care the method gives good results.

Electrolytic Attack.—The specimen is made the anode in a solution of an electrolyte, either by suspending it by a platinum wire or holding it in pliers wired to the positive pole of a battery. Electrolytes found suitable include ammonium nitrate, very dilute acids or ammonia for copper or brasses, sodium thiosulphate for bronzes, and dilute sulphuric acid to which hydrogen peroxide has been added for copper–nickel alloys. The current used is about 0·01 ampere per square centimetre, and the time occupied does not exceed 2 minutes.

√**Heat Tinting.**—The coloration of the different constituents of an alloy heated in air frequently differs considerably on account of variations in the rate at which they become covered with a film of oxide. The polished section is heated to about 120° C. on an iron plate to remove moisture, and whilst held by tongs, the warm section is very lightly rubbed on a soft piece of chamois leather. It is then placed on a layer of silver sand on an iron plate, or preferably floated in a crucible containing molten solder, and heated by a Bunsen burner. The heating of the specimen must be uniform; a temperature of 250° to 300° C. is suitable. Changes of

colour are watched, and when the specimen shows a general purple tint it is taken by the tongs and cooled in a bath of mercury.

The method is useful in the case of cast iron and some non-ferrous alloys such as bronzes. It is specially valuable in distinguishing certain constituents such as phosphides, but as considerable experience is required to obtain reliable results, it should only be used in conjunction with the usual methods of etching.

FIG. 6.—Section taken below the bottom of a drilled hole in 0·4 per cent. carbon steel, showing distortion of the constituents (ferrite and pearlite) produced by the severe mechanical work applied in drilling.

Etched with 1 per cent. nitric acid in alcohol. × 50.

FIG. 7.—Appearance of a microsection after leaving 00 emery paper. All scratches are in the same direction.

Unetched. × 100.

FIG. 8.—Section imperfectly prepared, showing dragging of the surface and forced polish.

Unetched. × 100.

FIG. 9.—The same section as in Fig. 8 etched with 5 per cent. nitric acid in alcohol. Scratches over which metal has flowed during polishing are revealed together with pits giving a false impression of the presence of inclusions. × 250.

FIG. 10.—The same specimen repolished, and etched with 5 per cent. nitric acid in alcohol. The material is "Armco" ingot iron, consisting of grains of ferrite. × 250.

PLATE I.

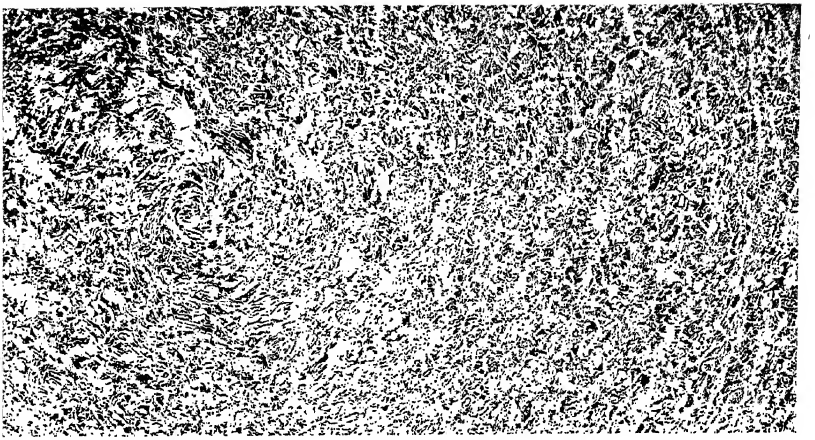


FIG. 6.

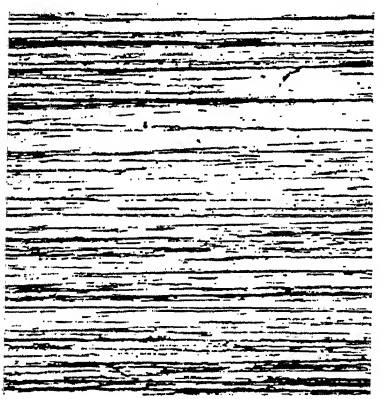


FIG. 7.

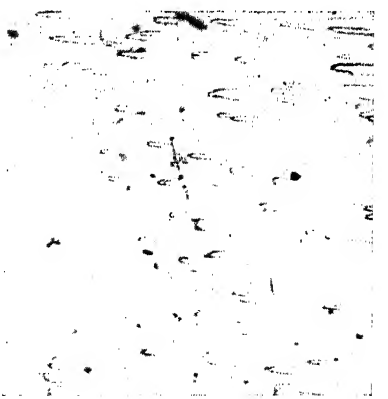


FIG. 8.

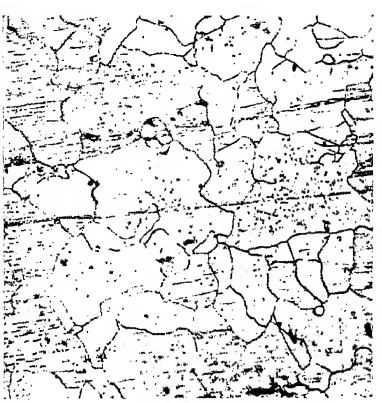


PLATE II.

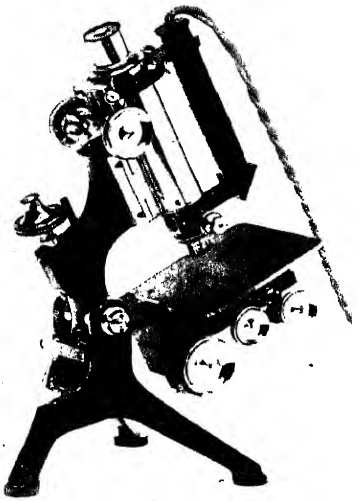


FIG. 11.

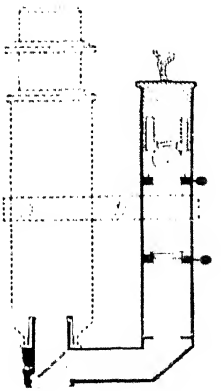


FIG. 12.

FIG. 13.

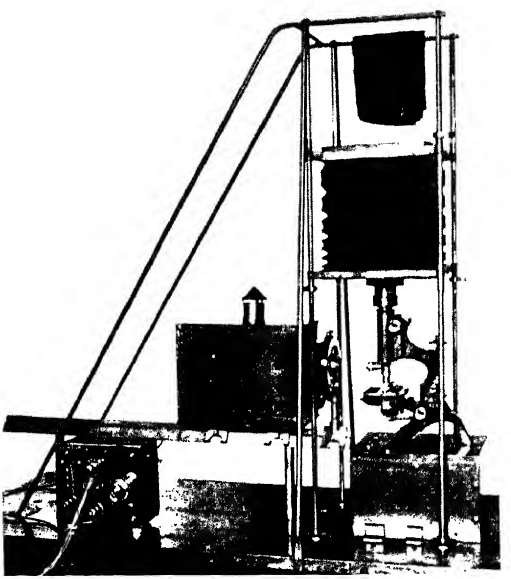


FIG. 14.

FIG. 11.—Metallurgical microscope by Messrs. Watson, with Beck Metallurgical Illuminator attached.

FIG. 12.—Sectional diagram of Beck Metallurgical Illuminator.

FIG. 13.—A simple illuminant for visual work. The wing nuts serve to adjust the height of the lamp from the bench, and the position of the disc relative to the filament of the lamp.

FIG. 14.—The apparatus shown was designed for general purposes, but primarily for metallurgical work. The whole of the illuminating system is mounted on a V bar which may be raised or lowered by means of a worm gear mounted on the underside of the bench. The beam may thus be brought into alignment with the vertical illuminator or with a substage mirror. The bench and the block on which the microscope rests are both very rigid, the latter being built up of steel plates.

The simple illuminating system shown in the diagram Fig. 17 is assembled.

CHAPTER III

THE MICROSCOPE AND METHOD OF MICROSCOPICAL EXAMINATION

THE optical system of the metallurgical microscope consists of two compound lenses, one near the object (known as the objective), and the other (the ocular) at a distance of from 6 to 10 inches from the objective. The objective produces an enlarged real image of a portion of the object under examination. For visual examination, the ocular is arranged to give a further enlarged virtual image of that produced by the objective; for photomicrography the ocular is arranged to project a further enlarged real image on to the screen or plate.

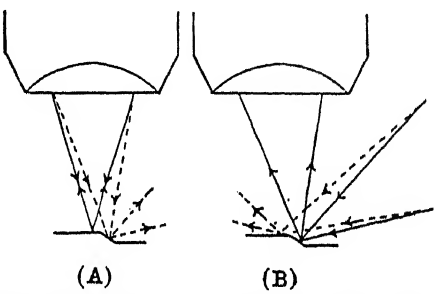


FIG. 15.—Diagrams illustrating (A) Vertical and (B) Oblique Illumination.

Metals are opaque to ordinary light, and have therefore to be examined by reflected light. For this reason the metallurgical microscope is usually not provided with the third lens system found on good microscopes designed for other classes of work, namely, the substage condenser, which serves to control the beam of light which illuminates a transparent object.

Illumination.—Proper illumination of the object is essential, otherwise the images produced by the microscope may be entirely misleading. There are two methods of illumination of metallurgical specimens, oblique and vertical (Fig. 15).

(a) *Oblique Illumination.*—The light is made to strike the

surface of the object from one direction or from various directions at an angle of less than 90°. Such rays falling on a perfectly smooth surface are reflected in a direction equally inclined to the normal and do not pass into the microscope tube, hence the surface appears black. Irregularities on the surface reflect light into the objective, giving bright lines or regions on a dark background.

Oblique illumination may be effected in various ways; for very low powers by ordinary daylight, or by artificial light focussed on to the surface by a lens or reflected on to the specimen by a parabolic reflector fitted to the objective; for higher magnifications by a hollow cone of light of wide angle focussed on to the specimen from an annular reflector or prism surrounding the objective. To study structure in relief at low magnifications it is sometimes convenient to illuminate the surface with beams of light of different colour coming from two or more directions. The symmetrical hollow cone of light is, however, more effective in illuminating all the contour and relief on the surface of the specimen, and is the only method available for high-power work on account of the closeness of the objective front to the specimen.

A full range of well-corrected objectives with self-contained ring illuminators by which hollow-cone dark-ground illumination is simply and very effectively obtained is now available, and with the advent of such facilities this method of illumination promises to be of much greater service in the future, though at present it is used chiefly at low magnifications for the examination of surface irregularities and inclusions.

(b) *Vertical Illumination.*—Most metallurgical microscopy is carried out with this type of illumination. A cone of light is made to fall perpendicularly on the surface of the object, being reflected back into the microscope from the smooth parts of the surface, but cast astray by any irregularities. The image produced by this method is, as regards light and shade, the reverse in general effect of that produced by oblique illumination.

To effect this type of illumination the cone of light travelling to and illuminating the object must traverse the same path as that reflected from it—that is, along the optic axis of the microscope. As at magnifications from 50 upwards there is not sufficient clearance between the object and the objective to permit of the insertion here of any illuminant or mirror, the incident beam of light is fed into the body tube of the microscope normal to the axis, and, by a reflector (or "vertical illuminator") placed behind the objective, is passed down through the objective and on to the surface of the specimen.

There are two types of vertical illuminator in general use, the prism and the glass slip type. The prism illuminator introduces an obstruction into the microscope tube which asymmetrically reduces the effective aperture of the objective with marked adverse effect on its image-forming quality. The glass slip illuminator is apt to produce more glare than the prism, thus tending to destroy contrast in the image, but this defect can be reduced by correct adjustment of the illuminating beam, and by proper selection of objectives. Under the best conditions, the glass slip illuminator gives a far more perfect image than the prism, and it should always be used for photography.

The beam of light is modified in character in passing through the objective, but as the optical constants of the objective, its focal length and aperture and also its distance from the specimen are all fixed by the image-forming requirements, control of the illumination must be effected entirely on the beam of light passed into the body tube. For clear and accurate portrayal of structure, critical control of illumination is essential. Briefly, by critical illumination is meant the provision of an illuminating cone of light which will enable the aperture of the objective to become effective, the accurate centration of this cone, and the removal from it of all stray light which would take no part in image formation.

If the object has a perfectly smooth surface of uniform colour, the real image produced at the focus of the ocular

will consist of an even disc of light. The ideal light source is a disc of the size of this image at a distance from the objective equal to that of the image, and emitting only a pencil of rays equivalent to that included within the lines AB.CD (Fig. 16). The aperture of the objective will only be fully utilised if any point E in the specimen produces a full cone of rays, EA.ED to be brought to an equivalent image point as at B; this necessitates the presence in the illuminating beam of rays corresponding to BD and CA. These rays will be present

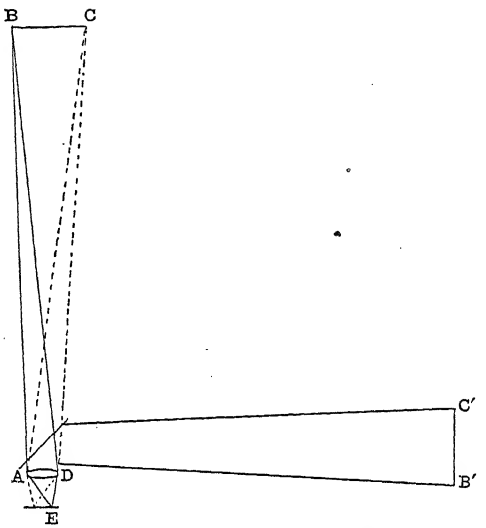


FIG. 16.—Diagram illustrating Critical Illumination.

if at B′C′ there is a self-luminous disc, or its equivalent such as an illuminated ground or opal glass disc. If, however, a lens is used, the provision of the requisite bundle of rays to utilise the aperture of the objective (and these only) is conditional on the light being brought sharply to a focus in the plane AD.

Under these conditions the disc of illumination corresponding to B′C′ will be sharply imaged by the objective on the surface of the specimen. If, then, a diaphragm is placed at B′C′ so as to reduce its size, the area of the illuminated portion of the specimen will be restricted without there being any

restriction of the full cone of light through the objective to any point in the still illuminated portion of the field, *i.e.* a diaphragm in the plane B′C′ acts purely as a field stop, without any restriction of aperture. The distance of this diaphragm from the back lens of the objective, B′A, should be equal to AB, the tube length of the microscope.

Improper control of the illuminating beam may result in restriction of the cone or pencil of rays necessary for the objective to work at its proper aperture, causing a reduction of resolving power and the production of spurious and distorted images. By the use of too wide or too strongly convergent a beam of light, rays other than those which form the image are reflected into the microscope and the image is spoilt.

Stray light, other than the true image-forming light, which passes along the microscope and is received by the ocular, whether produced by this or other causes, is spoken of as "glare."

Optical systems which fulfil the requirements for critical illumination are described in the section dealing with photomicrography, but if a separate bench microscope is used for visual work, the simple system described on page 32 may be fitted up on some suitable support, with a light source consisting of a circle about $\frac{1}{10}$ inch diameter of ground or opal glass illuminated by a 60-watt bulb of the gas-filled type, or a bulb of the motor head-lamp type placed close behind it.

Such a lighting system arranged alongside a bench microscope must always be kept accurately in alignment with the vertical illuminator. The microscope must not be disturbed in position, the tube may not be moved up or down, and all focussing must be done by the stage, the fine adjustment only being used to complete focussing at high powers.

These difficulties may be overcome by the use of a self-contained vertical illuminator attached to the body tube of the microscope. With such an illuminator in position the

tube may be racked up and down without disturbing the centring of the lighting, and any type of microscope without a focussing stage motion becomes adaptable for metallurgical work.

An illuminator of this type supplied by Messrs. Beck is shown in Figs. 11 and 12; it is designed so as not to be in the way of the hands whilst working, and to throw no harmful side strain on the body tube of the microscope. The illumination is provided by a 4-volt bulb of the pocket flash-lamp type which may be run from an accumulator or from the mains through a resistance, and is ample for visual work. The illumination is accurate and can be controlled by two properly located iris diaphragms, one in contact with the ground-glass disc which serves as light source regulating the aperture, and the other acting as field stop.

An illustration is given of the simplest form of illuminant for visual work (Fig. 13). The lamp is an ordinary metallic filament bulb of 40 or 50 watts behind a ground-glass screen. A rotatable disc containing a number of holes from $\frac{7}{8}$ to $\frac{1}{4}$ inch diameter allows the use of a disc of light, placed at tube-length distance from the mircoscope, of just sufficient size to illuminate the field of view at any magnification. Instead of the ring stop, an iris diaphragm may be fitted. No control of aperture is provided and a certain amount of stray light finds its way into the vertical illuminator, but as a simple light source this is greatly preferable to the practice of concentrating a strongly convergent beam from a bull's-eye lens into the microscope.

Mechanical Features of the Metallurgical Microscope.—As mentioned above, metallurgical microscopes as a rule carry no substage apparatus. It is desirable, however, that they should have a small hole in the stage itself and be so designed that substage fittings may be added if at any time it becomes necessary to examine transparent objects.

The stage should be so strongly constructed as to carry specimens of considerable weight without straining from the

normal, and rack and pinion traverse motions should be fitted into it. The coarse focussing of all metallurgical microscopes is effected by racking the stage itself to or from the objective, as any movement of the microscope tube throws the vertical illuminator out of alignment with the light source. The range of this stage focussing movement should be as long as possible, 4 inches is by no means too much, although more than 2 or 2½ inches is seldom provided; the variation in thickness of specimens, as well as the focussing distances of low-power objectives, have both to be covered by this movement.

The microscope should be perfectly stable and well balanced when clamped in any position between vertical and horizontal; the surface of the stage should be large and free from projections other than stage clips; even these should be removable, leaving a flat and open stage clear for the examination of large specimens.

Many objectives are computed to work with a tube length of 160 mm., and the body tube of the microscope should be sufficiently short for a vertical illuminator to be fitted without exceeding this 160 mm. overall length.

Objectives for Metallurgy.—All medium and high-power dry objectives for metallurgy should be corrected to work on uncovered objects. Oil-immersion objectives for biological work are, however, suitable for metallurgy, the absence of cover glass being compensated for by the film of oil. If the objectives are to be used with a prism type of illuminator, they should be mounted so that the back lens surface is nearly flush with the objective thread, otherwise it is impossible to obtain even illumination, as the prism itself when at any distance from the back lens acts as an irregular-shaped field stop.

In making a choice between the achromatic objectives, which are partially corrected for chromatic aberration, and the apochromats, which are more fully corrected, the following points should be borne in mind.

The apochromats as a class give the more perfect resolution

and central definition, but generally suffer to a somewhat greater extent than the achromats from curvature of field; in addition, they generally give rise to more glare over the image by reflections from their more numerous lens surfaces, and chiefly by pronounced reflection of the incident illuminating beam from the back lens surface, which is often relatively flat in the apochromatic objectives. If only visual work is to be undertaken, the achromats will certainly fulfil the requirements of all except the most experienced microscopist engaged in advanced research, and the expense of apochromats cannot be justified.

In selecting objectives it is better to make a photographic test as described on page 48 than to trust to visual impressions. For photographic work the ideal is a set of apochromatic objectives selected by an experienced photomicrographer for their comparative flatness of field and freedom from glare; these two faults which are often present in apochromats have a serious effect on the quality of photomicrographs. A range of achromats would probably give results in photographic work which are as good as, or better than, those given by a set of apochromats obtained by other than expert selection.

A selection of objectives to cover the requirements of visual and photographic work would include the following:

Achromatic; 50 mm., and 25 mm. or 16 mm.
Apochromatic or Achromatic; 12 mm. or 8 mm., 6 mm. or 4 mm., and 3 mm. or 2 mm.

It is desirable that, if possible, objectives be chosen having approximately similar tube lengths. A mixed set of lenses of the 160 to 180 mm. and 250 mm. tube-length types is inconvenient in visual work, and in photography leads to otherwise unnecessary changing of the illuminating system.

For magnifications of 1000 or over, an oil-immersion objective is used, a thin film of cedar-wood oil being introduced between the specimen and the objective. Since the working distance is small and the front lens is delicately

mounted, great care has to be exercised in focussing. When the objective has been screwed into position, one or two drops of immersion oil are applied to the surface of the specimen, and one drop also to the front lens of the objective. The stage is then racked up carefully until the two oil surfaces meet, the eye applied to the microscope and the stage very slowly racked further until the specimen comes roughly into focus, the final focussing being done by the fine adjustment. If the ocular is then removed, any air bubbles trapped in the oil film will be detected by looking down the microscope tube while slightly racking the specimen to and fro across the stage. If bubbles are seen, the process must be repeated until a film free from air is obtained.

Immersion oil varies in consistency; if rather thin the film is apt to break contact, particularly when the microscope tube is horizontal; if thick, tension in the film may lift the specimen a little during focussing, and allow it subsequently to settle back, unless the stage clips are kept strong and firm. Immersion oil is a drying and gumming oil, and it should never be allowed to remain on the objective or the specimen, also it should never be used to lubricate the microscope. After use the objective may be cleaned with a soft material such as an old well-washed silk handkerchief slightly moistened with saliva (which is just sufficiently alkaline to remove the oil). The front lenses of some immersion objectives are bezelled in, others depend to a greater or less degree on balsam for fixing, and the use of solvents such as alcohol or benzene (which may be used for cleaning the specimen) is therefore dangerous. If by chance a film of oil should become hardened on the objective, the smallest possible quantity of xylene on an old silk handkerchief should be used to remove it. A very effective substitute for cedar-wood oil consists of a mixture of a paraffin with monobromonaphthalene. The mixture has the same refractive index as cedar-wood oil, *viz.*—1·51, but is free from the tendency to gumming. Supplies are available through Messrs. Leitz.

Oculars.—The ordinary Huygenian oculars corrected for use with achromatic objectives are generally marked with a series number, which should not be confused with their magnifying power. The magnifying powers of the Zeiss Huygenian oculars are as follows:

Ocular number	1	2	3	4	5
Magnifying power	× 3	4	5·5	7	9

The "compensating" oculars used with apochromatic objectives are marked with numbers indicating their magnifying power. The most useful oculars are those of low and medium magnification, such as × 4 and × 8. An ocular of × 8 magnification will reveal clearly to a person of good eyesight all the detail resolved by most objectives, though a good objective of high aperture, used with critically controlled monochromatic illumination, may resolve detail too fine to be seen clearly except with an ocular of magnification × 18 or × 25.

Magnifications.—The linear magnification obtained in visual examination of an object may be determined approximately from the formula

$$L = \frac{T}{f} n$$

where T is the tube length of the microscope (measured from the eye lens of the ocular to the objective thread, and including the vertical illuminator),
f is the focal length of the objective,
n is the magnifying power of the ocular.

The formula is applicable with sufficient accuracy for visual work to all cases where the tube length is large in relation to the focal length of the objective, *i.e.* with a 160 mm. tube length it may be applied to objectives of 25 mm. focus and under.

Resolving Power.—Increased magnification without gain in resolving power is merely equivalent to the enlargement of a negative taken at smaller magnification by the same objective.

The resolving power of an objective, expressed as the minimum distance, δ, between two lines which can be resolved, is usually given by the formula:

$$\delta = \tfrac{1}{2}\lambda/\text{N.A.} = \tfrac{1}{2}\lambda/\mu \sin \alpha.$$

Where λ = the wave length of the light used;
N.A. = the numerical aperture of the objective;
α = one-half of the angular aperture, or apex angle of the cone of light entering the objective; and
μ = the refractive index of the medium between objective and specimen.

This equation refers to an object with a periodic structure like that of an optical grating: a different numerical coefficient of λ is applicable to the resolution of particles. It is not quantitatively applicable to metallographic structures, but correctly indicates that increased resolving power (diminution of δ) may be obtained by the use of an objective of high angular aperture, an immersion medium of high refractive index, and light of the shortest possible wave length.

Photomicrography.

For the purpose of obtaining photographs of the structures, the ocular of the microscope is made to serve as the lens of an ordinary bellows camera. Before the procedure followed in photomicrography is dealt with, the essential conditions which should govern methods of illumination and choice of equipment will be considered.

Illumination.—(1) A simple system which fulfils the requirements for critical illumination is shown in Fig. 17, where A represents the back lens of the objective, B the field lens, a condenser in a position corresponding to the plane B′C′ in Fig. 16 and C a small source of light. For simplicity the vertical-illuminator is omitted.

The distance AB is equal to the tube length of the microscope, and the objective A will project a sharp image of the lens disc B on to the surface of the specimen. The lens B is

chosen of such focal length that, when it is placed at tube-length distance from the objective A, and when the position of the illuminant C is suitably adjusted, it is possible to obtain a sharp image of C, of such a size as just, and only just, to fill the back lens A of the objective. If a lens of 2½ inch focus be used at B, then the image produced at A (using a tube length and distance AB of about 160 mm.) will be of just about the correct size to fill the back lens of a 2 mm. objective, with the 100 c.p. Pointolite as light source. When so adjusted, the system serves well for quite a range of work, the full aperture of the 2 mm. objective being used in order to obtain maximum resolution, whilst the medium power dry objectives (with back lenses as a rule slightly larger than the 2 mm.) have about two-thirds or three-quarters of their apertures filled.

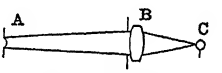


FIG. 17.—Simple Illuminating System for Photomicrography.

An iris fitted close to B acts purely as a field stop, and may always be adjusted so as to illuminate only the area on the specimen being photographed, thus reducing glare over the image without in any degree affecting the working aperture of the objective.

The above illuminating system is very simple and efficient, and as the number of optical components is reduced to a minimum, difficulties of centring and of securing alignment are almost eliminated; it may be used for the full range from the highest powers, down to work with a 25 mm. objective. (For powers below this, a different method of illumination is advised, to be described later.) The system just described provides no means of controlling the working apertures of the objectives. Such a control is very liable to abuse, apertures being restricted in order to obtain flatness of field to such an extent as materially to impair resolution and general quality of image. The system may therefore be regarded as a safe one, and the be-

DIFFICULTIES WHICH MAY BE EXPERIENCED BY THE BEGINNER IN PHOTOMICROGRAPHY WITH POSSIBLE CAUSES AND REMEDIES

Defect.	Cause.	Remedy.
Image on screen, or on developed plate, irregularly illuminated.	Condenser system not properly adjusted, or illuminant out of true alignment with it, or, Field lens not set at tube-length distance.	With illuminating system described on p. 35 (Fig. 18) field lens must be completely filled with light, and light must be brought to a sharp focus on it. If an arc lamp is used, care should be taken that the direct light from the crater, and not that from the wavering flame above it, is utilised. With the Pointolite, the creep of the electrode inside the bulb on heating must be allowed for before centring the light.
Negative too thin or too dense, flat and lacking in contrast.	Incorrect exposure, or faulty photographic technique. Glare from unsuitable objective will reduce contrast.	Expose successive strips of a plate at intervals and develop, noting which strip received correct exposure.
Small light patches (printing dark) on negative.	Dust, either on field lens or on ocular, or air bubbles in glass of field lens.	Rotate ocular to determine whether trouble is there or on field lens.
Dark blurred patches (printing light) on negative.	Stray light entering the camera, probably at connection between camera and microscope.	Carefully examine camera and dark slides for defects.
Image sharp on screen, but negative out of focus and blurred.	Inadequate water cooling of beam from an arc lamp. Vibration transmitted from camera to microscope in changing screen for dark slide.	Ease connection between microscope and camera.
	Fine adjustment creeping during exposure.	Slides of fine adjustment motion should be cleaned and re-lubricated, using finest clock oil. Fine focussing at high magnifications should be completed by motion in direction against the spring.
	Specimen moved on stage during exposure.	Strong stage springs are necessary with immersion objectives to overcome tension in oil film. Specimens may sag in a plasticine mounting when on a vertical stage.
	Blue rays not cut off, with achromatic objectives.	A suitable light filter must be used.
Image sharp in centre of negative, blurred all round; or sharp around, blurred in centre.	Incorrect focussing, or creeping of fine adjustment, or curvature of field of objective.	
Sharpness of negative falls off uniformly from one side of plate to the other.	Specimen not mounted dead flat.	Remount. Confirm source of trouble if necessary by focussing true flat plate.
An area on the screen which cannot be brought into really satisfactory sharp focus, to one side of the centre of the field (when using high-power objectives).	The illumination of the objective aperture will be found to be eccentric.	Carefully re-centre, and if any re-centring of field is then required, again check aperture lighting after making it.
Fine scratches or other defects on specimen showing prominently on negative.	Such defects usually prominent in negative, although scarcely noticeable when viewing the screen. Reducing the aperture of objective always accentuates such markings.	Re-prepare specimen. Use full aperture of objective. Scratches are more readily noticed if, whilst viewing the focussing screen, the stage is slightly racked across to cause the field to move.
General imperfect definition, with immersion objective.	Air bubbles in oil film.	Re-oil and re-focus.
No image on plate, but general fogging (when using immersion objective).	Film of oil broken during or just before exposure.	Add oil and re-focus.

ginner in photomicrography is advised to fit it up if possible after the manner shown in Fig. 14, and with this apparatus in use, following the procedure described on pages 43 to 52 to overcome most of the technicalities of micrography, such as adjustments of the optical system, elimination of glare, choice of photographic materials, etc. In this connection, a few of the difficulties which may be experienced, with possible causes and remedies, are given on the opposite page. At a later stage the choice of objectives by photographic tests, correction of tube-length settings and other delicate operations may be carried out, preferably with the illuminating system now to be described.

(2) A more elaborate illuminating system for photographic work which permits aperture control is shown in Fig. 18.

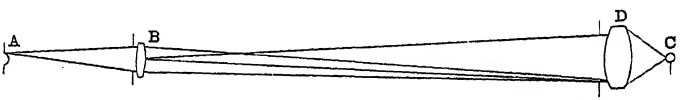


FIG. 18.—A More Elaborate System Giving Independent Control of Aperture and Field.

Here A is the back lens of the objective, B the field lens, C the illuminant and D an additional condenser lens. The distance AB must again be tube-length distance, whilst BD may conveniently be about 20 inches. The lens B now focusses a sharp image of lens D on to A, and, as the iris in D is adjusted, the size of the illuminated disc at A, and therefore the working aperture of the objective, may be controlled.

The lens B must now be of 5 inch to $5\frac{1}{4}$ inch focus (for use with objectives corrected for 160 mm. tube length). The objective A will as before focus a sharp image of lens B and its iris on to the specimen, so that it becomes necessary for the lens B to be quite evenly illuminated, and if this is to be done without wastage of light, the lens D must focus a sharp image of C on to the lens B, of size such as just to cover the full aperture of B (this needs to be about $\frac{7}{8}$ inch diameter).

The brilliance of illumination obtainable is largely dependent on lens D; its iris diaphragm will, in general, be open to an

mercury arc, should be available for direct illumination and critical high-power work.

Though the older forms of mercury lamp were unsuitable for metallography, on account of their low intrinsic intensity, the more recent high-pressure type is suitable for all work on which a Pointolite can be used. As made by The General Electric Company under the name "Osira," the lamp has an outer frosted bulb, which is removed by leading a crack round its neck, revealing a small discharge tube of quartz (Fig. 39), from which intense monochromatic light, either blue, green or yellow, is available by a suitable choice of filters. The 80-watt lamp, run from standard A.C. voltages through a small transformer and choke, has given no trouble in the course of several years' constant use, and is considered to be the most efficient light source for precision micrographic work yet available.

Colour Screens.—With a glass slip illuminator, well-chosen objectives and properly controlled illumination, there should be quite sufficient contrast in the image for photographic purposes, and it should seldom be necessary to select colour filters for the purpose of increasing contrast; rather, in some cases, it may be desirable to reduce contrast. Thus, copper alloys, when etched to show their grain structure with some grains darkened, are apt to give excessive contrast, and for these a deep yellow or red filter may advantageously be used.

With achromatic objectives a colour screen which will filter blue and blue-violet rays from the light must be used, otherwise sharp pictures are not obtainable. For general work with these or with apochromats, a yellow-green filter is very suitable, giving a tone rendering of any colour present in the specimen approximating to that seen visually in the light of a metal filament lamp. Some apochromats will give sharp photographs without any colour filter when used with a Pointolite, whilst others require the removal of the blue-violet, a light yellow filter being sufficient. A blue-green filter may be used to obtain the increased resolving power of

the shorter wave-length light. As blue-green light is of rather low visual intensity, the uncertainty of focussing by it may introduce some error, and it may be found advisable to focus by the unscreened light when working on dark subjects. With a well-corrected apochromat it should then be possible to insert the blue-green filter without causing any change of focus. It is, however, desirable to check this and, if necessary, to make the final adjustment by the aid of a focussing magnifier on a clear glass screen with the filter in position.

The appropriate filters for use with the mercury lamp are referred to on p. 50. Both achromats and apochromats yield their sharpest definition and highest resolution when used with the deep-blue radiation from this source, but the correct tube-length setting will in most cases be found to be 10 or 15 mm. shorter than the normal setting, and focussing must be done in the blue light.

Apparatus for Photomicrography.—This may be divided roughly into two classes :—

(*a*) The more elaborate outfits (Metallographs), comprising an inverted microscope, and fitted with reflecting prisms or mirrors so that the illuminating train, microscope body, and camera may all be mounted in easily accessible and comfortable working positions; and

(*b*) the simpler type in which an ordinary microscope, as used for visual work, is employed.

The first type of apparatus is generally very convenient for medium- and high-power work, and when a large amount of work, from 50 diameters upwards, has to be done, the comfort and speed in working which it furnishes are appreciable. The provision for illumination at very low powers is efficient in several of the newer outfits, but some upsetting of the normal assembly of apparatus is inevitable, and maintenance of a separate outfit, designed specially for low-power work, might in some instances be worth consideration.

In selecting an outfit of this type, with the knowledge that most of the work will be done under vertical illumination at medium and high powers, attention should be given to certain details. All lenses and reflecting surfaces should be easily accessible for cleaning, and small parts which are to be removed for this purpose should be so mounted as to ensure accurate replacement. A mirror introduced between the ocular and camera screen is liable to impair some part of the image. If such an arrangement is essential for convenient working, a mirror of optically worked glass, silvered on the surface and covered with a very thin glass plate, is probably the best alternative to an uninterrupted path. A delicate and reliable fine adjustment is essential: in general, the smaller the weight of the parts set in motion by the fine adjustment the more sensitive it will be and the longer life it will give. Objectives to be used with some outfits need to be specially corrected in accordance with the considerably increased effective tube length of the microscope; as a consequence only the one maker's objectives may be available, and this imposes an undesirable limitation of choice. To obtain the best results, use of a steady source of light such as the Pointolite or high-pressure mercury lamp should be permissible, though an arc lamp as an alternative is desirable if dark-ground illumination is to be employed. Elaboration of the optical system by reflecting prisms and mirrors may so reduce the intensity of the image as to make illumination by Pointolite inadequate and compel the use of an arc lamp.

An image with an extensive flat field, obtained by reducing the working aperture of the objective and demonstrated under the powerful illumination of an arc lamp, though fascinating to an inexperienced observer, may be highly imperfect. The illuminating system should admit of independent control of field and aperture lighting and should enable the back lenses of the objectives to be properly filled with light. The optical equipment is, or should be, a matter of separate choice and, if best results are to be obtained from the selected objectives,

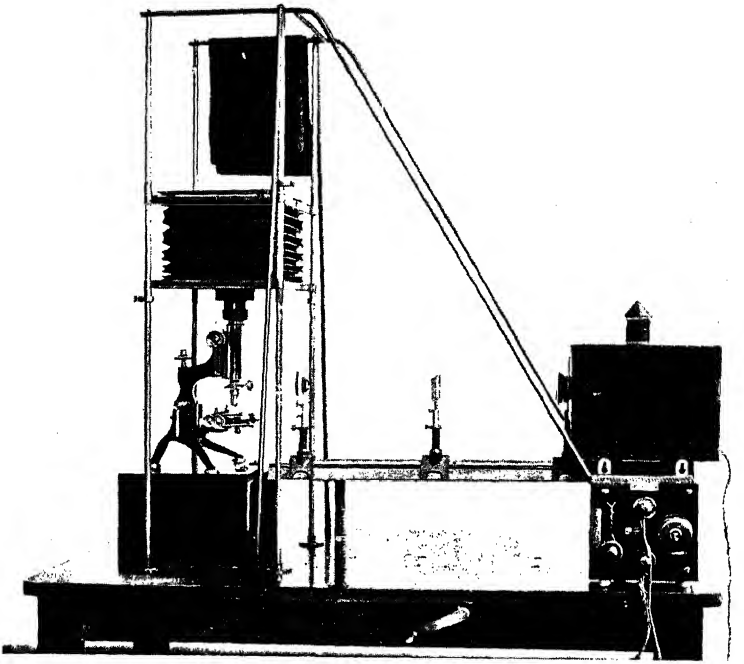


FIG. 19.—Photomicrographic apparatus, with the illuminating system of FIG. 18 assembled.

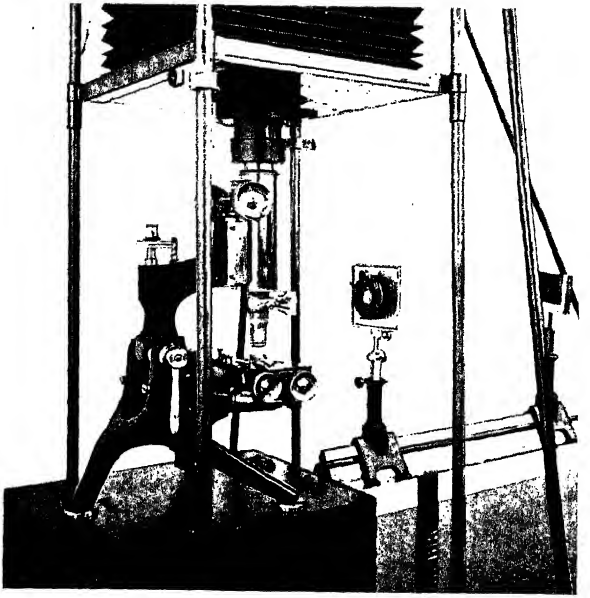


FIG. 20.—A view showing the frame support for the field lens and shutter, which allows of a crosswise centring adjustment.

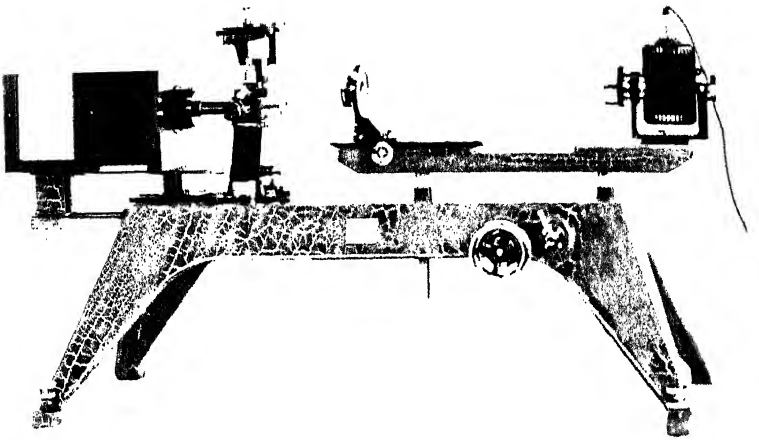


FIG. 21. Photomicrographic Equipment.

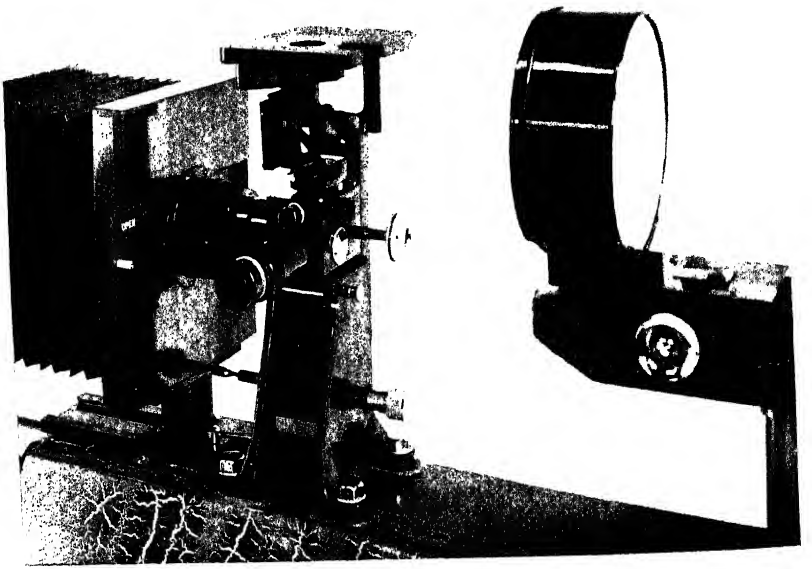


FIG. 22.—Method of illumination for low-power photomicrography.

means to vary the tube length, and to focus the lighting accordingly, must be provided.

Equipment designed in the Research Department, Woolwich,* to incorporate these features, and made by Messrs. Beck, is shown in Figs. 21 and 22. The illuminating train, which can provide critical illumination on metal specimens over a range of magnifications from 4 to 2,500 diameters, is carried on a bar which may be brought into line with the usual vertical illuminator or with transparent reflectors fitted to the fronts of the micro-anastigmats used for low-power work in accordance with the principles described in Chapter IV. The illuminating train may also be raised still higher when a focussing substage and mirror are fitted for the micrography of transparent materials. Each interchangeable condenser is mounted so that it may be removed and replaced with no disturbance of its centration. The camera is of the reflex type with variable extension. The image is first thrown by the reflex mirror in the camera on to the ground-glass screen which faces the operator when he is seated beside the instrument. When the field has been chosen the mirror is swung out of position, and the final focussing and exposure are carried out at the back of the camera. Provision is made for the use of oblique illumination and polarised light. The source of light usually employed is the high-pressure mercury lamp.

The simpler type of outfit is cheaper, and where total expenditure is limited, allows of a more extensive or high-grade optical equipment being obtained. The apparatus which has been used for the production of many of the micrographs reproduced in this book is shown in Figs. 14, 19 and 20. The camera is a whole-plate square bellows, sliding on four tubular steel supports. There is no long-distance focussing adjustment, the milled head on the microscope being within reach. The bench, and the block on which the microscope rests, are both very rigid, the latter being built of thick

* *Journ. Royal Micros. Soc.*, 1935, vol. lv, p. 79.

steel plates. The outfit is stable and immune from vibration owing chiefly to this substantial stand for the microscope. The lenses used in the condenser train are mounted on saddle stands having a small cross-wise centring adjustment, which, together with the sliding pillar of the stand, permits accurate centration of each lens.

The only novel feature of the apparatus is the V bar on which the condenser train is mounted. This may be raised or lowered by a worm gear operating underneath the table, and so may be brought into alignment with the vertical illuminator at any position of the microscope body tube—a very useful feature in low-power work, when the body tube needs to be racked up to its highest position to provide enough focussing distance for low-power objectives.

The outfit is conveniently adaptable to the changes in the illuminating train required for very low-power work, to tube-length adjustments, or to whatever variations in equipment or practice may be required. Continuous and rapid work with the vertical camera is tiring; but where a high standard of work is the prime consideration, an outfit of this type may be adopted with confidence.

Oculars for Photomicrography.—The "Projection" oculars are specially computed for photographic work and may be used with either achromatic or apochromatic objectives. They are generally made with a low magnifying power (indicated by a number with which they are marked), and they therefore require a rather long camera extension, involving the use of a long-distance focussing adjustment with its uncertainties. The most effective position of the upper lens of the projection ocular depends on its distance from the screen on which the image is projected, and is indicated on a tape-measure supplied with the ocular. The lens is then adjusted by screwing in or out until the arrow it bears coincides with the required position on a graduated dial.

In practice excellent results are obtainable by the use of Huygenian or of compensating oculars, of moderate magnify-

ing power, with achromatic or apochromatic objectives respectively; the fine focussing adjustment of the microscope is then within reach. A range of oculars from × 4 to × 10 should be available in both Huygenian and compensating types, with, in addition, one or two compensating oculars of higher magnification.

The additional curvature of field introduced by oculars is quite negligible, *i.e.* all the curvature shown on the camera screen may be attributed to curvature in the primary image given by the objective. Recently a number of oculars have been placed on the market in which an attempt has been made to compensate for the curved field of the objective; with some of these the central definition has been impaired.

Testing of the Apparatus and Optical Equipment.—The correct assembly and adjustment of the outfit should be checked by making a number of tests, some of which may afterwards occasionally be repeated. The exact procedure in testing and in operation will vary to some extent with the type of apparatus employed, but the following notes may be regarded as directly applicable to the simpler type of outfit just described.

A specimen showing lamellar pearlite, rather lightly etched and very carefully levelled in plasticine on a glass slip, may be placed on the stage and the light switched on. If a Pointolite is in use, two or three minutes should be allowed for the electrode inside the bulb to come to rest, and then an examination made to see that the bulb is so turned that the glowing electrode is as near as possible to the condenser lens without either of the wire supports in the bulb being in the path of the light. The various condenser lenses in the illuminating train must be centred by measurement (as accurately as possible to the same height), and then the Pointolite adjusted in position in its lamp house so as to project a beam centrally through the system. A medium-power objective (16 mm.), and low-power ocular having been fitted, a dark colour screen is placed in the screen holder so that the eye may not be

damaged by too bright a light, and the specimen brought into view by focussing; the glass slip of the illuminator may need adjustment. Adjustments to the iris diaphragms and to the positions of the lenses in the illuminating train may now be made in accordance with conditions already laid down; the field lens must be quite evenly filled with light, there should be a sharp image of the glowing Pointolite electrode thrown on the mount holding the field lens and slightly overlapping the lens itself in size; light must also be brought to a focus by the field lens in the plane of the back lens of the objective. The ocular should be removed and the back lens of the objective inspected for centrality of lighting (a small micrometer adjustment to the position of the field lens is useful for this centration), then the eyepiece replaced, the field stop reduced and the centrality of the field lighting adjusted by movement of the glass slip of the vertical illuminator. After this has been done, the centration of aperture lighting may require a further slight readjustment.

After adjustment of the aperture control (when the illuminating system permits) so that about two-thirds to three-quarters of the back lens of the objective is filled with light, the ocular may be replaced and the field brought into focus on the camera screen. With the field iris partly closed, the field lens should now be moved to and fro until the image of its iris is in focus on the screen along with that of the specimen; if the focal length of the field lens has been correctly chosen, only very slight, if any, adjustment from the previous setting to give sharp light focus on the back of the objective should be required.

The image on the screen should be examined for stationary black specks which do not move when the specimen is racked across the stage. The source of any such specks will be found either on the ocular or on the field lens; the joint of the camera should be eased away a little and the ocular rotated. If the specks move, the ocular must be taken to pieces and cleaned; if they remain stationary, the field lens should be

examined for dust or for tiny air bubbles in the glass of its lenses; if any defects are sufficiently prominent to remain visible on the screen with a very slight mis-setting of the field lens, the lens must be changed for another free from air bubbles.

The objective may now be changed to a 4 mm., the specimen focussed and the field iris opened until the full field of the ocular is in view on the screen. After some one point on the periphery of the field has been focussed carefully, the whole rim of the field should be examined for evenness of focus. Any irregularity will be due either to the specimen not being mounted flat, or to the microscope stage being out of true. If there is trouble of this kind, a small flat steel plate about $3 \times 1 \times \frac{1}{8}$ inch, and of perfectly uniform thickness, may be used as a test plate; one surface should have fine emery scratches over it and these are brought to a focus on the screen. Any asymmetry of focus must now be due to the stage itself. The test should be repeated with a weight of four or six ounces, in addition to the test plate, resting on the stage. Irregularity of focus on the screen is not likely to be due to mis-alignment of the camera, as slight displacement there is without noticeable effect on the focus.

The pearlitic specimen should now be focussed by the 4 mm. objective, the centre of the field this time being brought into sharp focus, and the centrality of the illumination over the back lens of the objective should be checked by inspection. Whilst some one point in the image is observed, the fine adjustment should be turned to and fro so as to run through the focus. Provided the specimen is accurately level and normal to the microscope axis and the illumination central, any appreciable lateral shift of the image whilst running through the focus indicates lateral shift of the objective and must be remedied by the microscope-maker.

After re-focussing the centre of field the instrument may be left for ten minutes or more; if there is any shift in the focus this is due to creep, and must be corrected. Long-

distance fine focussing adjustments are notorious for this trouble, but inadequate water-cooling of the beam of light from a powerful arc lamp may cause a similar effect.

The operations of exposing a plate (*i.e.* removing the ground-glass screen, fitting a dark slide and drawing its shutter) should be gone through to determine whether they cause a disturbance of the focus. Such disturbance is most likely to be caused by direct transmittance of vibration from the camera to the microscope itself; direct rigid contact between the camera and the microscope should be avoided if possible.

Magnifications.—The camera extensions required for the various magnifications may next be determined. A stage micrometer scale engraved on invar is brought into focus with each objective in turn and the camera extension adjusted and oculars selected so that the appropriate magnification on the screen is obtained in each case. Care must be taken that the prescribed tube length is employed for each objective in turn.

By the use of objectives working with tube lengths of 160 to 200 mm., the magnifications given below will all be obtainable with an extension from ocular to screen of between 25 and 45 cms.

Magnification .	50	100	250	500	1000
Objective .	25 mm.	16 mm.	8 mm.	4mm.	2mm.
Ocular .	× 4	× 7	× 7	× 7	× 7

Standard magnifications such as those given above should be used.

Routine Procedure in Photographing a Structure.—The specimen having been mounted on the microscope and the light turned on, the image is focussed on the screen, which is set to the proper distance to obtain the magnification desired with the objective and ocular selected. With the field iris wide open a check may be made of the level mounting of the specimen as already described, after which the field iris is closed until the illuminated circle on the screen is only slightly

larger than necessary to cover the plate to be used; this will be found to reduce glare on the image and give better contrast in the photograph.

With the aid of a focussing magnifier, the image of the field selected is brought to a sharp focus at a point midway between the centre and the corner of the rectangle to be photographed. The focussing should always be completed by a motion which is against the spring of the fine adjustment in order to minimise any danger of creep. A small cover-glass should be cemented to the ground side of the focussing screen by a little balsam or immersion oil at the above-mentioned point of critical focus; it will allow the image to be picked up more brightly by a focussing magnifier.

Exposure.—Provided that a steady light source such as the Pointolite is used, it will be found that exposures can, to quite a considerable extent, be standardised.

A simple change of objective from low to high power will have little effect on the intensity of illumination on the screen. Exposure required will vary as the square of the ocular power and as the square of the camera extension. In a case of magnifications of 100 and 500 obtained as follows:—

× 100	16 mm. objective	× 7 ocular	Camera 24 cms.
× 500	4 mm.	× 6	40

the relative exposure at × 500 will be:-

$$\left(\frac{40 \times 6}{24 \times 7}\right)^2 = 2{\cdot}04, \text{ or twice, approximately.}$$

The aperture-controlling diaphragm may be calibrated, numbers 5, 4, 3, 2, 1, being given to a series of apertures whose diameters are in the ratio 4, 2·8, 2, 1·4, 1, and so arranged that the middle number of the range is applied to the aperture most commonly to be used, namely, that which will two-thirds to three-quarters fill the back of the medium-power objectives. Each step in aperture number will represent a halving of the exposure, and if that required with a given plate and colour filter and a specimen of average character be

determined at × 100 and taken as standard, a table may be drawn up as below:—

Magnification.	Objective.	Ocular.	Camera extension.	Exposure with aperture diaphragm: 1.	2.	3.	4.	5.
× 100	16 mm.	7	24 cm.	4	2	1	½	¼
× 500	4 ,,	6	40 ,,	8	4	2	1	½
× 1000	3 ,,	14	30 ,,	24	12	6	3	1·5

The relative exposures for various colour filters and plates may be determined, and their factors, combined with the above, will give a close estimate of exposure, the one uncertain factor being the reflecting power of the specimen.

Test exposures may be made by exposing plates in strips, withdrawing the shutter of the dark slide an inch or so at a time, and if a record of the results be kept, the exposure problem should soon be mastered.

Photographic Materials.—For nearly all subjects, plates of the "screened chromatic" type (some makes of which are much faster to yellow-green light than others, although of similar speed to daylight) should give ample contrast. Occasionally a flat subject, or one showing fine dark lines on a brilliant ground, may require a more contrasty plate, such as the "chromatic ordinary," but really hard "Process" plates should not be required. In the absence of red coloration, panchromatic plates are unnecessary. For use with monochromatic blue light (mercury lamp), the Ilford "Fast Blue Sensitive" plate has been found very suitable. The relative exposures for the various grades of plates, used in conjunction with the different colour screens, must be determined by tests.

Photographic Tests of Objectives.—In the design of any micro-objective, flatness of field is obtainable only by some sacrifice of central definition. A compromise has therefore to be effected, and in the case of apochromats the computer strives as a rule to meet the requirements of the pure research worker by giving the best possible central definition. Such fine definition is very easily destroyed by mal-adjustment of light-

PLATE V.

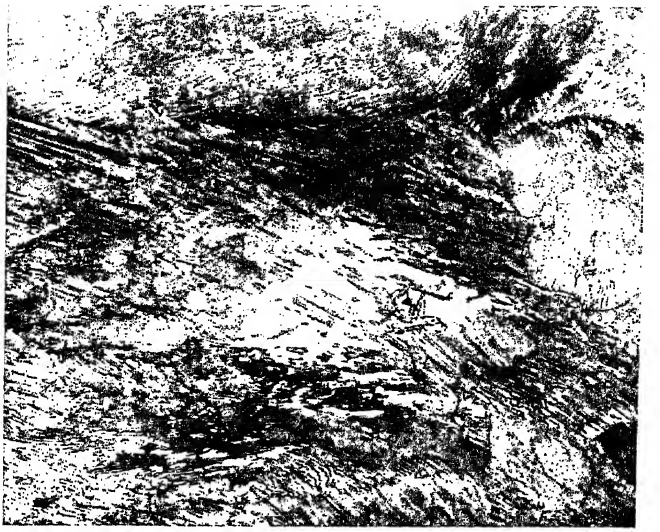


FIG. 23.

FIG. 24.

FIGS. 23 and 24.—Lamellar pearlite and ferrite. 4 mm. Apochromat. × 500.

Micrographs showing the importance of tube-length correction, Fig. 23 being obtained with a tube length of 180 mm. (makers' setting) and Fig. 24 with tube length of 200 mm.

[*Facing p.* 48.

PLATE VI.

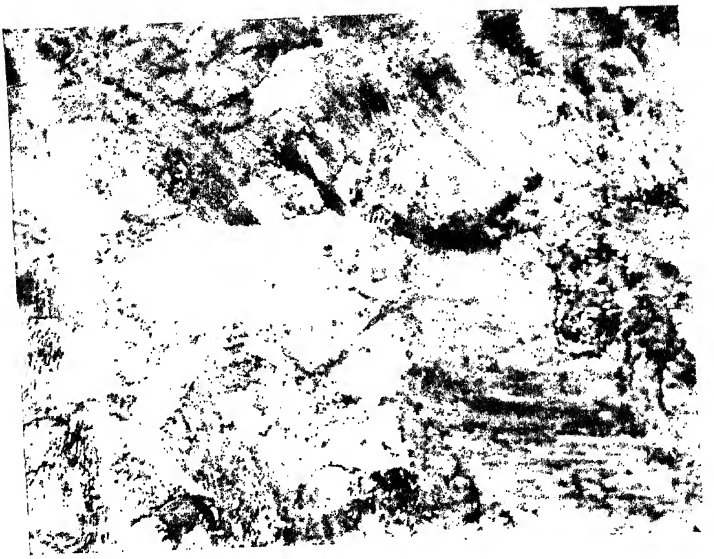


FIG. 25. ·3 mm. Apochromat. N.A. 1.30.

FIG. 26.—2 mm. Apochromat. N.A. 1.30.

FIGS. 25 and 26.—Fine lamellar and sorbitic pearlite. × 1000

ing conditions or by using the objective with even a slightly inaccurate tube-length setting; it follows that the utmost care is required if the best selection is to be made among apochromatic, or the higher power achromatic objectives.

With suitable oculars and the camera arranged to give magnifications with the various objectives in accordance with the table on page 46, a sharp field should be obtainable over a $2\frac{1}{2}$ to 3 inch circle. Any reasonably good objective, except perhaps a 2 mm., should give this without undue restriction of aperture; a lens with a more curved field can scarcely be regarded as suitable for general photomicrographic work, as exquisite central definition does not overcome the bad appearance of blurred edges. The back lens of the objectives should be kept regularly under observation in the course of test for their selection, and at least two-thirds to three-quarters of their apertures filled, and the lighting carefully centred.

A specimen showing fine lamellar pearlite in steel, quite lightly etched, is a suitable test object, since with a light etching and fine structure glare over the image is more noticeable. A useful comparison may be made by removing the specimen from the microscope and fitting various objectives, the light reflected to the screen by them under these conditions is glare; in some cases its quantity is surprising, and obviously a most important point in selection.

The excellence of the colour corrections is, for metallurgical work, a point of minor relative importance; most metallurgical specimens are monochromatic in character, and the yellow to green light for which most achromats are corrected is very suitable for nearly all work. Careful attention should be given to the setting of the tube length, the makers' figure being accepted unless some experience has been gained in its experimental determination. A small error in this setting may cause a splendid objective to be overlooked (see Figs. 23 and 24). The desirability of selecting a series of objectives of fairly uniform tube lengths, so as to avoid the necessity of making changes in the illuminating system, should be borne

Micrographs illustrating the performance of a 4 mm. Apochromat, N.A. 0·95, with monochromatic light from a mercury lamp as illuminant.

Magnification 500 diameters.

The specimen of pearlite was focussed on the screen in the green light of the mercury lamp, and then photographed in the following order, without movement of the focussing mechanism, by light of different colours, obtained by inserting the appropriate screen:

	Light.	*Wave Length.*	*Wratten Filter.*
Fig. 27	Blue	4359 Å	47 (Tri-colour blue) + 2A
Fig. 28	Yellow	5780 Å	22
Fig. 29	Green	5460 Å	77A

Although the third photograph taken showed that the initial focussing in green light was correct and unchanged, the photograph taken in the blue light was badly out of focus, indicating that the colour correction even of an apochromat is not sufficiently wide to include the blue of the mercury lamp, which is so far removed in wave length from the visually strong rays.

FIG. 30.—Refocussed in blue light. Finer definition is given by an image focussed and photographed in blue light, a somewhat shorter tube length being employed.

In occasional instances, as in the photography of multi-coloured specimens for which the use of mono-chromatic radiation may not be desirable, a Wratten 12 ("minus blue") filter may be used. This cuts off the blue radiation and permits of photography with the mixture of green and yellow, giving tonal effects similar to those seen by eye.

PLATE VII.

FIG. 27.

FIG. 28.

FIG. 29.

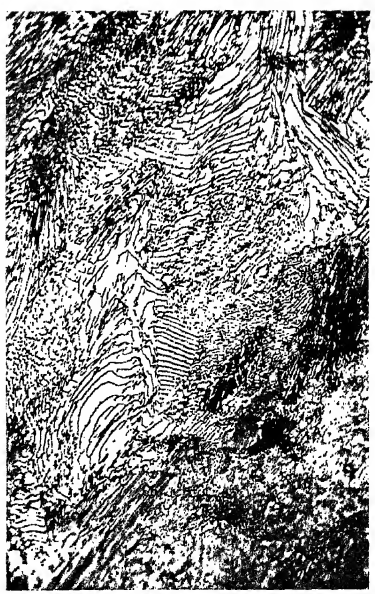


FIG. 30.

[*Facing p.* 50.

PLATE VIII.

FIG. 31.

FIG. 32.

FIG. 33.

FIG. 34

Micrographs taken with Achromatic Objectives.

FIG. 31.—α and β solid solutions in cast brass containing copper 60, zinc 39, tin 1 per cent.

× 50. 25 mm. objective.

FIG. 32.—Ferrite and pearlite in an annealed chromium steel containing carbon 0·35, chromium 1·5 per cent.

× 250. 8 mm. objective.

FIG. 33.—Coalesced carbide and ferrite in nickel steel (carbon 0·30, nickel 5·2 per cent.), annealed and very slowly cooled.

× 500. 4 mm. objective.

FIG. 34.—Fine lamellar pearlite.

× 1000. 2 mm. objective.

in mind, but should not be permitted to cause the rejection of any objective of outstanding merit.

A good 2 mm. apochromat may probably have a very restricted flat field, and in consequence give more satisfactory photographs when used at × 1500 or × 2000 than at × 1000. For this latter magnification a 3 mm. immersion objective may be used to give a more satisfactory flat field, particularly if its aperture be a little restricted, but some slight loss of resolving power as compared with the 2 mm. objective will probably occur; some 3 mm. objectives have a very flat field, but the resolution they give may not be appreciably better than that of a good 4 mm. dry lens. Examples of the work of good 3 mm. and 2 mm. apochromatic objectives are shown in Figs. 25 and 26; and Figs. 27 to 30 illustrate the performance of a 4 mm. apochromat with monochromatic light from a mercury lamp as illuminant. When different high-power apochromats are examined under proper working conditions the definition and resolution which they give is generally excellent and the choice among them will probably be decided by absence of glare.

The achromatic objectives are less exacting in the matter of critical operating conditions than the apochromats, and thoroughly satisfactory work is possible with them. A range of micrographs taken with achromats is shown in Figs. 31 to 34, in addition to many others in the text of later chapters.

Tube-length Correction.—When some proficiency in photomicrography has been obtained, the tube-length settings for the various objectives in use should be checked, as the makers' figures must not be accepted as strictly applicable to each individual objective used in conjunction with different oculars and light filters. The higher the numerical aperture of the objective and the more perfect its correction for spherical aberration the more sensitive it will be to variations of tube length. A true comparison of high-grade objectives is not possible unless made with the correct tube-length adjustment for each in turn. A specimen showing the finest detail the

objective is capable of resolving should be photographed with the ocular and light filter intended to be used, first with the makers' tube-length setting and then with settings a little on either side of that judged to be correct. A suitable subject to use in determining tube-length setting is a minute speck or inclusion in the centre of a field of the lightly etched ferrite of a normalised or annealed low-carbon steel. It may be observed by means of a focussing magnifier on the clear glass camera screen while changes in tube length are made and the image re-focussed, but the final test must be made photographically. At the correct setting not only do the first-observed inclusions appear sharpest, but others, smaller or more removed from the centre, may come into view. For this test it is essential that the fine adjustment of the microscope should be quite free from creep: the illumination must be accurately centred and re-focussed as changes in tube length are made. The field stop should be adjusted to illuminate only the central zone of the ocular, and the aperture control set so that the aperture of the objective is just filled with light.

Certain makers have recently adopted an infinity tube-length setting for their objectives, an additional converging lens being fitted into the body-tube of the microscope; this has the advantage of permitting parallel, in place of convergent, rays to be passed through the illuminator plate. This method, however, is also liable to slight error, which requires correction if the system is to gain in perfection of definition.

Microscopy with Deep-blue Light.—To take maximum advantage of the increased resolution obtainable by the use of the deep-blue light ($\lambda = 4359$ Å) of the mercury lamp, a monochromatic immersion objective of N.A. 1·60 has been computed for metallurgical work by R. J. Bracey of the British Scientific Instruments Research Association, and made by Messrs. Beck.* Micrographs taken with this objective are shown in Figs. 38 and 219. The immersion fluid used is monobromonaphthalene (refractive index, 1·66) which may

* *Journ. Royal Micros. Soc.*, 1933, vol. liii, p. 328.

be removed from the specimen by means of acetone. The objective is free from glare and gives a resolution of about 180,000 lines per inch. Although designed as a monochromat it is sufficiently achromatic to give excellent definition when used with the blue band of radiation given by a Pointolite through a Wratten 50 L filter. For visual examination with this objective a green filter and a slightly increased tube length may be used, with either a Pointolite or mercury lamp as source of light.

Microscopy with Ultra-violet Light.—This method, which has proved to be so successful in biological and medical research, has been applied to metallurgical specimens.*

A quartz prism is used to separate from either the cadmium or the magnesium spark a beam of ultra-violet light of approximately half the wave length of blue visual light, and by its use the theoretical resolving power, attainable with objectives of similar numerical aperture, is doubled. The whole optical system of the apparatus must be of quartz or other material transparent to ultra-violet light, and as the image is invisible, other means of focussing are necessary, calling for the utmost precision and skill. The quartz objectives at present available were computed for bacteriological work without any special attempt to avoid the flat lens surfaces which may introduce glare in metallurgical micrography. The highest numerical aperture they possess, viz. about 1·3, is low compared with that of the 1·6 N.A. monochromat described above. By the use of these objectives on metal specimens increase of resolving power in accordance with theory has been obtained, and no unforeseen difficulties have been encountered. There appears to be no fundamental obstacle to the production of ultra-violet light objectives of high numerical aperture, specially designed for metallurgical purposes.

* F. F. Lucas, *Journ. Franklin Inst.*, 1934, vol. ccvii, p. 661; J. Smiles and H. Wrighton, *Proc. Roy. Soc.*, 1937, vol. A. clviii, p. 671.

CHAPTER IV

LOW-POWER PHOTOMICROGRAPHY AND MACROGRAPHY

THERE is often much to be learned from micro-examination at quite low powers; a better idea of the quantity and distribution of inclusions and of cavities is obtainable, and the relation between the true microstructure and the primary crystallisation, or macro-structure, of the metal may best be studied at low magnification. In order that these structures may be observed and recorded effectively, it is necessary to apply "vertical illumination": the appearance and the photographs may then readily be correlated with those obtained at higher magnifications.

The images obtained at quite low magnifications, when low-power micro-objectives are used with the systems of vertical illumination described in the previous chapter, are not entirely satisfactory chiefly owing to the amount of glare set up by the large and flat back lens of the objective. The glare may be reduced to some extent by the use of a prism type illuminator, or by restriction of working aperture, but in either case there is generally a resultant blurring of the image of any surface irregularities such as slag inclusions or cracks and some unevenness of illumination. These imperfections may be tolerated in visual examination. They are not sufficiently serious to merit the fitting up of special equipment on the microscope, and low-power visual examinations may be made by using micro-objectives of 50 or 75 mm. focal length a low-power ocular, and, if contrast is weak in the image, a prism illuminator.

The method of calculating visual magnification given in the previous chapter is not applicable to long-focus objectives.

In the case of a 75 mm. (3-inch) objective, for instance, the initial magnification when used with a 6-inch tube length is not $\frac{6}{3} = 2$, but something much lower. Assuming the primary image to be produced 6 inches from the objective, and applying the formula for conjugate foci

$$\frac{1}{f_1} + \frac{1}{f_2} = \frac{1}{f}$$

where f_1 and f_2 are object and image distances and f is the focal length, it is seen that the object distance must also be 6 inches, and therefore primary magnification is 1.

A point of more direct importance is that with most microscopes it is impossible to obtain a separation of 6 inches between objective and specimen, and an image may only be formed in the microscope with objectives of this focal length by extending the draw tube to its limit of ten inches or more.

For photographic purposes, objectives of the photographic anastigmat or Planar type may be used with advantage. These lenses cover a larger area on the specimen, and have a flatter field than micro-objectives of equivalent focus; they also have a sufficient free working distance to allow of the use of a glass slip reflector between objective and specimen, thereby almost eliminating glare. They must be used without an ocular.

With the vertical illuminator placed between objective and specimen, the objective takes no part in controlling the illumination; this and other considerations necessitate a modified illuminating system. At low magnifications, the area under observation on the specimen becomes large in relation to the front lens of the objective. The conditions of vertical illumination at higher magnifications are shown in Fig. 35, where the field in view is small in relation to the objective front AB, and may be represented by a point C. Light transmitted through the objective along the path AC will be reflected into the objective along CB and vice versa,

every point on the objective front thus receiving light from C. With light transmitted through the objective at low powers a similar condition holds only with regard to the centre of the field, and if the extremities of a field BC (Fig. 36) are to reflect light into the whole objective front, and the field thereby be evenly illuminated, a cone of light must be pro-

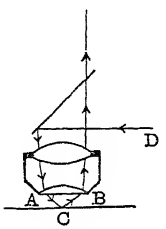


FIG. 35.—Vertical Illumination at High Powers.

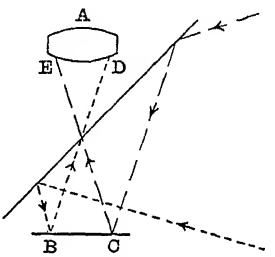


FIG. 36.—Vertical Illumination at Low Powers.

vided which is sufficiently wide to allow rays corresponding to BD and CE to be reflected to the objective.

The arrangement shown in Figs. 37 and 41 is suitable for photography at magnifications between × 25 and × 10, the area illuminated being sufficient to fill a quarter-plate. The required wide-angled cone of light is provided by a large aperture photographic lens of $4\frac{3}{4}$ inch focus and $f3$ aperture

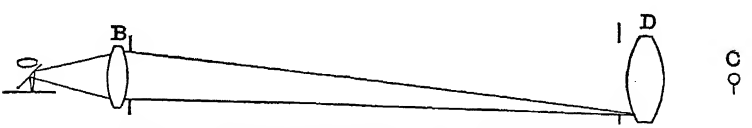


FIG. 37.—Illuminating System for Low Magnifications.

at B, and in order that a sufficiently large area on the specimen may be illuminated, the lens D, which is the one by Swift mentioned on page 36, must be opened to its full aperture of $1\frac{3}{4}$ inch.

Results showing a rather exceptional combination of large flat field with good resolution are obtainable at magnifications from 15 to 25 diameters by the use of one of the modern baby-ciné anastigmat lens of about $\frac{7}{8}$ inch focus and $f2$ aperture. Such a lens, for micrographic purposes, must be mounted the

FIG. 38.—Sorbite in an oil-hardened and tempered nickel-chromium steel, showing the granular structure of the carbide and a minute film of included matter (running vertically near the middle of the photograph).

Etched with nitric acid in alcohol. × 2500.

This micrograph was taken with a monochromat, N.A. 1·60, in blue light ($\lambda = 4350$ Å), the immersion fluid being monobromonaphthalene ($\mu = 1{\cdot}66$).

FIG. 39.—High-pressure mercury lamp (G.E.C. "Osira") with outer bulb removed, as used as an illuminant in photomicrographic work. Half actual size.

FIG. 40.—Hyper-eutectoid steel (carbon 1·2 per cent.) as cast. Photographed with $\frac{7}{8}$ inch ciné lens, and showing the large flat field obtainable. × 20.

The black circle shows the field covered by a $\frac{7}{8}$-inch micro-objective as usually employed to cover a 3-inch circle at 50 magnifications.

PLATE IX.

FIG. 38.

FIG. 39.

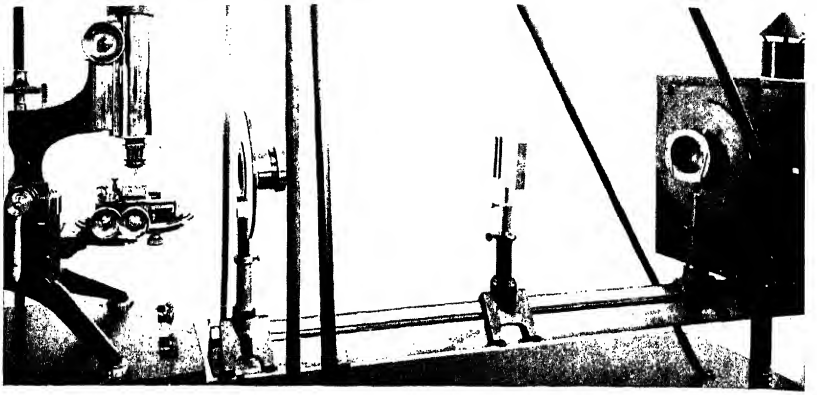


FIG. 41.—Illuminating system used with $\frac{7}{8}$ inch ciné lens and 35 mm. micro anastigmat. (Magnifications of 25 to 10 diameters.)

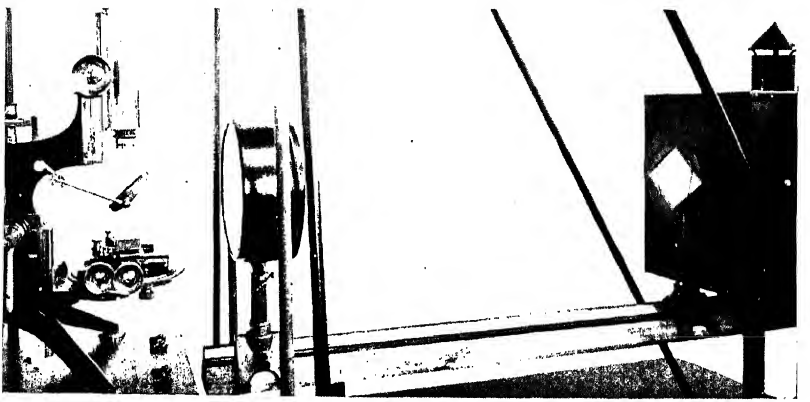


FIG. 42.—Illuminating system used with 75 mm. micro-anastigmat. (Magnification of 5 diameters.)

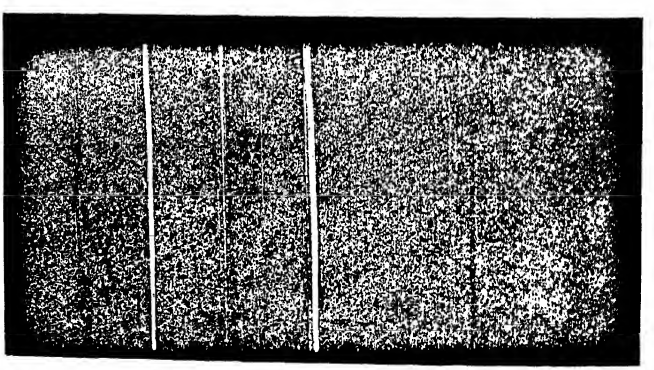


FIG. 43.—Longitudinal section of forged 0·5 per cent. carbon steel showing ghosts. × 5. 77 mm. micro-anastigmat. Vertical illumination as shown in Figs. 37 and 42.

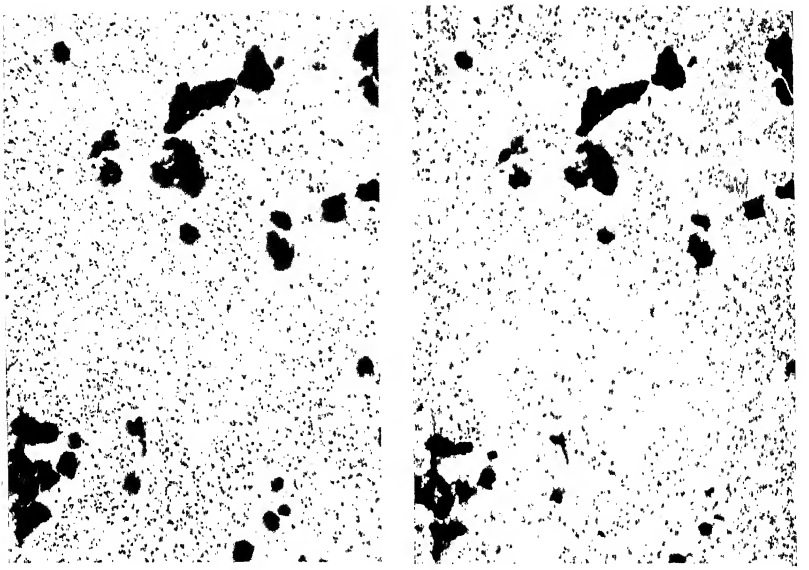
opposite way about to that used for ordinary photography, *i.e.* with what is normally the front surface of the lens facing into the camera; this must always be done so that the correction for spherical aberration in the lens may not be vitiated. With the condenser system shown in Figs. 37 and 41, almost the whole of the aperture of the lens may be filled (corresponding to a numerical aperture of about 0·22). The resolution thus obtainable is almost equivalent to that normally obtained with a micro-objective as used for photographs at 50 or 100 magnifications. The definition obtained, whilst not so critical as the central definition of a good micro-objective, is good enough to give a thoroughly satisfactory image at the low magnification employed; it is given over a very much larger flat field, and in addition, the portrayal of cracks and cavities is more accurate (Figs. 40, 44 and 45). The vertical illuminator is a glass cover-slip of $\frac{3}{4}$ to 1 inch diameter, mounted so that a rotating motion may be obtained, in a small bracket held in place by the objective collar. The draw tube of the microscope is removed in order not to restrict the field, and a light-tight connection arranged between the wide body tube and the camera front.

The iris diaphragm on lens B (Fig. 37) acts as aperture control, and that on D as field stop. It will be found necessary to centre the illumination accurately, and this may be most quickly carried out as follows. Lenses B and D are arranged in alignment as nearly as possible and set so that the beam of light impinges centrally on the glass slip illuminator. With both iris diaphragms open the specimen is brought roughly into focus, and then B is adjusted axially so that an image of D is focussed on the surface of the specimen. D is next adjusted so that the rays from it fill, or almost fill, the lens B. Some further slight adjustment of B may now be required in order to obtain a sharp and even disc of light on the surface of the specimen; this may best be done by the aid of a small slip of white paper temporarily placed on the specimen so that the illumination there may be readily observed. If the back of

the objective is now observed (the paper having been removed), it will probably be found that the illumination there is not central, and this should next be corrected by turning the glass slip illuminator until the spot of light on the back lens is central. Finally the field illumination should be centred by almost closing the iris of D so that only a small portion of the field on the screen is illuminated and bringing this to a central position by slight lateral adjustment of lens B in its supporting frame; after which, on opening both irises the full field of view should be evenly illuminated and also practically the whole aperture of the objective.

An objective of this type is sufficiently achromatised to work well without a colour filter, but it will be found that, with the illuminating system described, the image on the screen is very brilliant, and shows enough contrast to demand the use of rather soft-working (and therefore somewhat rapid) photographic plates. Exposures without a colour filter are apt to be inconveniently short; with a light yellow-green filter they may be only of the order of two to four seconds.

The assumption has been made, in this and the previous chapter, that the surface of a metal specimen, as polished and etched for micro-examination, acts sufficiently as a true reflector to permit of proper aperture control in metallurgical microscopy. If the surface were sufficiently roughened by the etching to cause it to break up and reflect light in all directions, and thereby cause the specimen to act in some degree as a self-luminous object, regulation of the character of the incident beam of light would be valueless. It is of interest to examine the back of the $\frac{7}{8}$-inch lens, in use as above described, whilst it is in focus on a moderately etched specimen. If the specimen were spreading its light so as to utilise the full aperture of the objective independently of the character of the incident beam, then the back of the objective should remain evenly illuminated when the incident beam is restricted by closing the diaphragm in B. This is far from the case, the illuminated portion of the objective aperture will be found to



(*a*) (*b*)

FIG. 44.—Cavities in steel casting. × 25.

(*a*) Taken with 40 mm. micro-objective. Note enlarged and blurred appearance of surface irregularities.
(*b*) Taken with $\frac{7}{8}$ inch ciné lens.

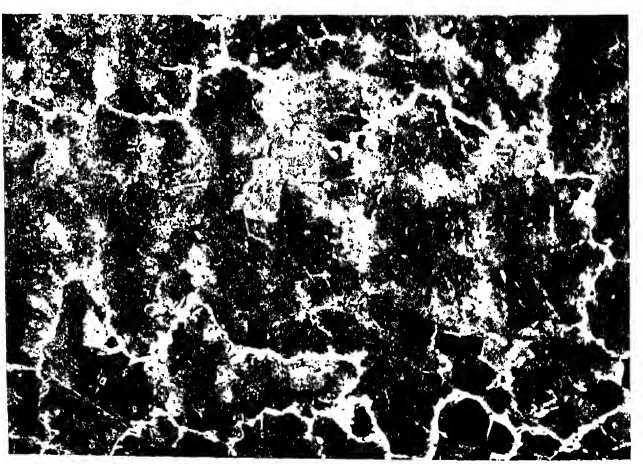


FIG. 45.—From steel ingot.
× 15. $\frac{7}{8}$ inch ciné lens.
Illustrating the definition obtained and covering power of the lens.

[*Facing p.* 61.

be sharply defined and to vary in accordance with the angle of the incident light.

At lower magnifications the area on the specimen to be illuminated becomes still larger, and in order to produce a focussed disc of light of the requisite size, the lens B (Figs. 37 and 42) must be of greater focal length, and also of large diameter to preserve the wide angled cone.

It will be found that the rays from D will by no means fill this condenser; a piece of ground glass is accordingly fixed close in front of D; the whole area of B is now able to pick up light from this new radiant surface, and the requirements of wide-angled cone with focussed light disc of sufficient diameter are met. There is great loss of light at the ground glass, but still there is ample intensity for comfortable examination of the screen image. For a magnification of ten diameters a photo-anastigmat or Planar of 35 mm. focal length will be suitable; for five diameters a 75 mm. lens of a similar type may be used. For field searching with these objectives in use, a low-power ocular may be employed in an extended draw tube. The image will, however, be somewhat imperfect as the corrections are spoilt, and the field brought into view by a low-power ocular of standard pattern is considerably smaller than that available on the screen.

A larger glass slip illuminator will be required at these lowest powers; in the photograph, Fig. 42, a framed glass disc of about 1½ inch diameter mounted in gymbals is shown bracketed to the limb of the microscope; this is a very convenient mounting, as either the specimen or the objective may be racked up or down to focus without disturbance to the lighting system.

Oblique illumination at low magnifications may be effected by the light of a small electric lamp directed through a bull's-eye or similar condensing lens on to the surface of the specimen; or two such lamps may be used, one from either side. With specimens showing relief, the angle of the illumination should be adjusted, and the specimen rotated until a suitable shadow effect is obtained.

Photography of Macrostructures

The term "macrostructure" embraces all the range of features of metal surfaces, from those just visible to the eye, but more comfortably examined with the aid of a hand magnifier, to the whole surface of a large ingot or forging; it includes all patterns, either in colour or relief, or both, related to the structure of the metal, and also all markings indicative of unsoundness, cracking, segregation or other imperfections in the metal.

The portrayal of these structures calls for a technique quite different from that used in the commercial photography of objects, metal or otherwise, for such purposes as catalogue illustrations in which design and shape must be faithfully reproduced, and surface marks or irregularities are generally to be regarded as blemishes, and suppressed in the photograph. In the photography of macrostructures the external shape is a matter of minor importance (it may already have been partly or wholly destroyed by cutting), but surface features must be reproduced in all possible detail and in a uniform manner over the whole of the area included in the photograph.

Visual examination of a macro-etched surface of quite moderate dimensions in a room, by the light of one or two windows, will indicate that with a fixed viewpoint and stationary specimen, a uniform appearance over the whole of the surface is only obtainable by attention to the lighting, for some part of the surface, which happens to catch the light of a window and reflect it direct to the eye, may present an image appearance quite different from that of the remainder. A slight change of viewpoint or movement of the specimen will cause a re-arrangement of the lighting, and indeed, in examining a macrosection, this turning of the head or specimen is done without thought, so as to observe the effects of light reflected at different angles, and the various visual impressions are mentally summed up. Further, in making a visual examination, two eyes are used, and the stereoscopic effect

PLATE XII.

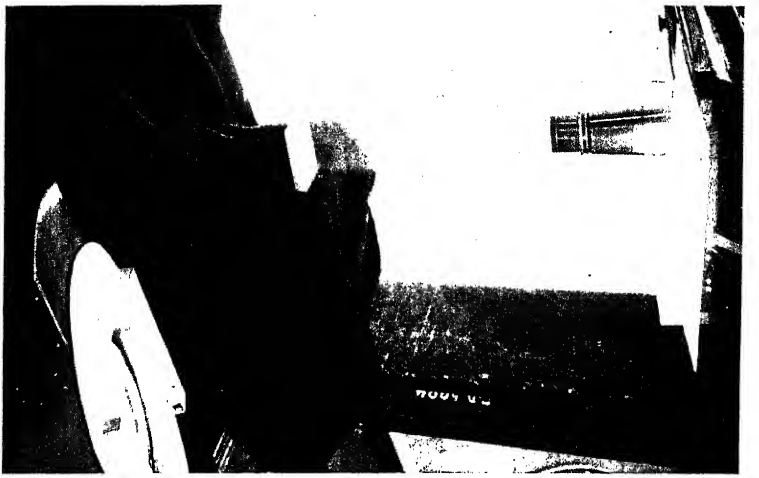


FIG. 46.

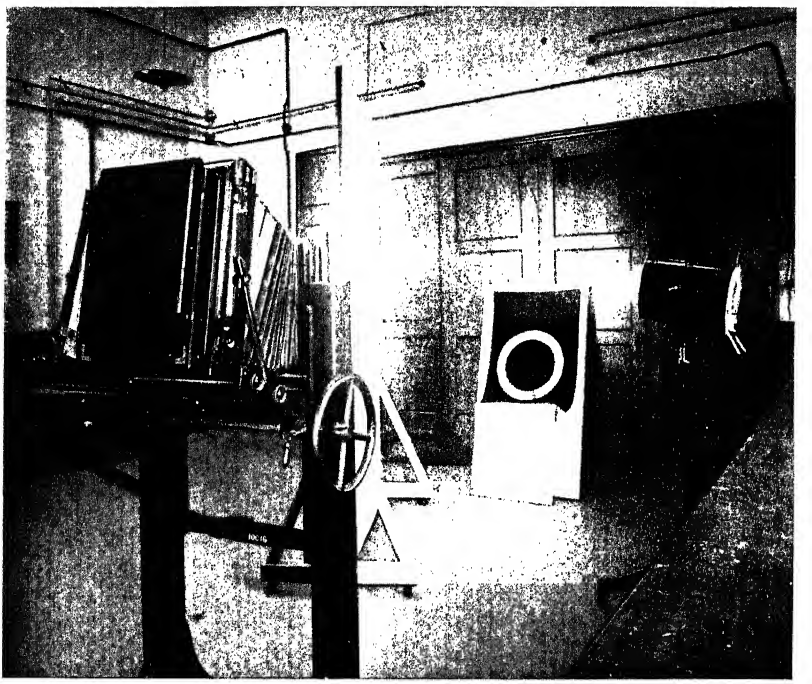


FIG. 47.

FIGS 46 and 47.—Showing arrangements of apparatus for obtaining the equivalent of "vertical illumination" in photo-macrography.

[*Facing p.* 62.

gives prompt differentiation between dark but smooth features and cavities or cracks.

The one eye of the camera cannot entirely overcome the absence of stereoscopic relief, but, on the other hand, by the provision of suitable illumination, uniform in character over the whole surface from the viewpoint of the lens and chosen to accentuate structural features, the photographer may be able to reveal the details of a macrosection in a completely satisfactory manner.

Equipment.—A half-plate square bellows "studio" camera with double extension will be found suitable for this work. A rigid tripod with tilting and rotating top, extension rise, and with the legs cross braced so as to prevent slip, will be required when large objects are being photographed, whilst something in the nature of a copying table may conveniently be used for fixing up smaller specimens in front of the camera.

Two projector lamps of the "focuslite" type, with gas-filled cluster filament bulbs of 250 or 500 watts, will provide convenient means of illumination; their light may be concentrated or spread over larger areas as required.

A set of three or four photographic objectives covering a range of 3 inch to about 12 inch focus is necessary; these should be anastigmats, but need not be of very large aperture, *f*8 being sufficient. They may very probably be selected from the stocks of second-hand photographic dealers provided that they may be had on approval for testing.

The chief precaution which must be taken when choosing a lens for this work is that it should be reasonably free from spherical aberration when projecting an approximately actual-sized image. Photographic lenses are normally computed to be clear of this defect when photographing relatively distant objects, this being the manner in which they are most commonly used, with the distance from lens to camera screen approximately equal to the focal length of the lens. The degree to which this correction is maintained when the lens-

to-image distance is increased, varies considerably in different types of lenses. When a lens is used to give a well-magnified image of an object, lens-to-image distance is increased, and object-to-lens distance is reduced almost to focal length; the trouble may then be avoided simply by turning the lens round, but for producing approximately actual size images, when object-to-lens and lens-to-image distances are more or less equal and well in excess of the focal length, this expedient is not available.

If a new set of lenses is to be obtained, attention should be given to those made specially for copying and known as "Process" anastigmats, as they are suitably corrected in this respect. Their other corrections also are generally of a high order and they are rather expensive, but otherwise ideal for the work. Lenses which will meet the requirements may be selected as follows:—

A sheet of fine and clear printing is set up in front of the camera, quite normal to the camera axis and parallel to the focussing screen, and strongly illuminated by the projector lamps. Its image is obtained at approximately actual size and carefully focussed, by the aid of a focussing magnifier with the lens at full aperture. The aperture should then be reduced to *f*22 or *f*32 and, whilst the image on the centre of the screen is observed through the magnifier, the camera screen should be slowly racked back a little farther from the lens. If the image seen at small aperture is noticeably improved in sharpness by racking back, the lens is not entirely suitable, and a further choice should be made.

With photographic lenses, as distinct from micro-objectives, definition of fine detail may often be improved by restriction of aperture, and as some depth of focus is frequently required and prolongation of exposure is a matter of little consequence, a rather small lens aperture is often employed. The image on the screen is seldom sufficiently bright for focussing, however, at small apertures, hence the necessity for lenses free from spherical aberration under actual working

conditions, so that there shall be no change in focus when the aperture is reduced.

Among anastigmats, only those of very early make are likely to be unsatisfactory in other respects, such as lack of covering power, or curvature of field.

The photography of macrostructures is best carried out in a rather large room, with large windows on two or more sides and roof lights, so that a good diffuse illumination is obtainable. Dark blinds or shutters should be fitted so that the room may be darkened, and, as light is apt to be reflected by polished or smooth surfaces from even quite narrow streaks along the edge of a blind, causing puzzling irregular illumination, the blinds should be well fitting.

The methods of illumination employed may be roughly divided into the two classes of oblique and vertical.

Oblique Illumination gives as a rule an appearance similar to that seen under diffuse daylight. Its effects may be accentuated with artificial lighting by projecting the light at a very wide angle from the normal, or by illuminating the specimen from one direction only, whereby small cavities or irregularities in a surface will remain unilluminated, whilst the fine relief patterns produced by rather strong etching on some macrostructures will be thrown into light and shade.

Polished surfaces, or those which remain smooth after etching, will reflect oblique light clear of the camera lens and so appear dark in the photograph. Surfaces which on etching reveal their structure by the production of a light and dark, or coloured, patina, may be more satisfactorily photographed under vertical illumination.

For oblique illumination the camera should be normal to, and opposite the centre of, the surface to be photographed. There is no perspective to be preserved, and therefore a lens of relatively short focus may be used, with the object of getting near to the surface and picking up the fine detail more clearly; the lens should, however, cover the size of the

plate, at the magnification employed, reasonably sharply to the corners and without falling off of illumination there.

For the photography of large surfaces, such as an ingot section some 3 feet in extent, on a half-plate, a lens of about 9 inches focus would be suitable, whereas for copying actual size, a lens of 6 to 7 inches focus should cover the half-plate sharply and evenly; for a magnification of two diameters a 4- or 5-inch lens is suitable, and a 3-inch lens of the micro-anastigmat or Planar type will cover the plate at magnifications of four or five diameters. The micro-anastigmats have their corrections adjusted and their components suitably mounted for use in this way, that is, with a relatively long distance between lens and plate and a short distance, approximating to the focal length, between lens and specimen. If a short-focus lens, designed for a small amateur or a ciné camera, is used, it should be mounted the opposite way about on the camera front, with what is normally the front lens pointing inwards to the plate.

Short-focus lenses bring the camera front very close to the specimen, where it is apt to interfere with illumination; a conical sleeve lens adaptor as shown in Fig. 46 is useful in such cases.

When the position of the camera has been approximately adjusted to give the image desired on the screen, the camera back may be pushed forward near to the lens panel, the focussing screen removed and the lens unscrewed from its flange, so that the eye may be placed close behind and a view-point nearly the same as that of the lens obtained. The appearance of the surface may be studied under the diffuse illumination of the room and also by the light of one or more projector lamps set at varying angles; any altered appearance given by the lamps may as a rule be enhanced by darkening the room.

Vertical Illumination.—The appearance of a polished and etched macrosection which shows, on a coarse scale, constituent features related to those which are customarily

viewed under the microscope, is, when seen under oblique illumination, difficult and tedious to interpret or to correlate with microstructure. In steel specimens, for example, ferrite veins appear dark and fine cracks light and the one may easily be taken for the other (Figs. 50 and 51). Further, the finer detail of such a structure may not be made visible at all, since it is produced by a patina or colour, rather than by a relief effect.

Although it is impracticable to provide an axial and sufficiently large cone of light to give true "vertical illumination" over the surfaces of macrospecimens, a system of illumination is available which produces quite a similar appearance. Owing to the great covering power of photographic lenses as compared with micro-objectives, the specimen, lens and screen may be set up well out of alignment with one another and yet allow non-axial light to be reflected to the lens from smooth portions of the surface, thus securing the equivalent of vertical illumination.

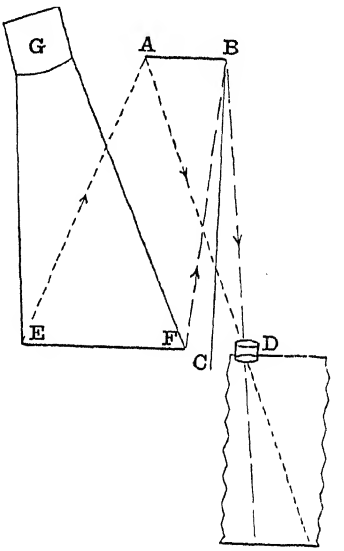


FIG. 48.—Diagram showing Method of obtaining the Equivalent of "Vertical Illumination" in the Photography of Macrosections.

In Fig. 48, AB is a macrosection, and D the camera lens in a position slightly beyond the line BC, which is the normal to the surface at B. Light to be reflected into the camera lens from smooth portions of the surface near B must be incident along the path FB, and from portions near A, along EA. If an area with a surface not too smooth, but with good reflecting properties, such as white blotting-paper or a white distempered board, at EF be strongly illuminated as by a projector placed at G, the whole surface of AB will be illuminated in the required manner. The image produced by the

Photographs illustrating the advantage of vertical illumination in interpreting macrostructures and in correlating them with microstructures. Etched with nitric acid in alcohol.

FIG. 49.—Section from a steel ingot. Ferrite and Pearlite. "Vertical illumination": photograph, actual size.

FIG. 50.—Portion of section from steel ingot. Oblique illumination. Ferrite dark. × 2.

FIG. 51.—The same. Vertical illumination. Ferrite light. × 2.

FIG. 52.—Portion of section from steel ingot. Vertical illumination. × 5.

FIG. 53.—Cast electrolytic copper, showing allotriomorphic grains of copper, with some globules of cuprous oxide.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 54.—Rolled and annealed copper. Polyhedral grains of copper showing some twinning, with globules of cuprous oxide (oxygen 0·08 per cent.).
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 55.—Cast nickel, showing allotriomorphic grains of nickel with some inclusions of oxide and graphite.
Etched with a 2 : 1 : 1 mixture of nitric acid, acetic acid and water. × 100.

FIG. 56.—Lead, extruded hot. Polyhedral grains of lead with inclusions.
Etched with acetic acid and hydrogen peroxide. × 15.

FIG. 57.—Dead mild steel, carbon 0·05 per cent., annealed at 930° C. and slowly cooled, then reheated to 660° C. and quenched in water. The grain size is unaffected by this reheating, and the carbon is held in solid solution by the quenching.
Etched with 5 per cent. nitric acid in alcohol. × 100.

FIG. 58.—Mild steel, carbon 0·1 per cent., reheated to 880° C. and cooled quickly, showing refinement of grain size which occurs on recrystallisation at the Ac_3 point.
Etched with 5 per cent. nitric acid in alcohol. × 100.

lens will be out of centre on the screen if the camera is placed parallel to the normal BC. The cross front movement of the camera should be used as indicated so as to bring the image on to the focussing screen whilst maintaining camera front and focussing screen both parallel to AB; in this way distortion is avoided. If, with the whole of the cross front movement in use, the image cannot be completely brought on to the screen, an attempt should be made to reduce the distance FD to a minimum, which will permit the object AB being brought a little more into alignment with the camera. If moved too far, however, the illumination of B on the camera screen may be weakened in comparison with A. Alternatively, the camera may be turned to face a little more directly towards AB; some distortion of the image of AB on the screen may then be noticeable, but as a rule this is of no consequence. The aperture of the lens may need to be considerably reduced to bring the whole of the image sharply into focus, or the swing back of the camera may be used; this will introduce some further slight distortion, but the maximum distortion likely to be produced is quite insufficient to be of consequence in relation to macrostructure or its interpretation.

The illumination is not critical; an irregular portion of the surface near B may throw some light it receives from E into the lens, but in practice a very satisfactory image is produced with ample contrast for photography, provided that the area EF is regulated to the minimum necessary to cover AB, and that diffuse illumination is removed by darkening the room.

No light from the projector must be allowed to strike the lens. A shade may be fitted to the lens to ensure this.

The size of the bright surface EF will depend on the size of the specimen and its distance away. If placed alongside the camera lens, EF will require to be approximately twice the size of AB, and it should be also of approximately the same shape, so that it may be kept of minimum area, for

crispness and contrast in the image are largely dependent on this. Strips of black cloth or paper may be pinned over the white board to bring the shape of the white reflecting area roughly into conformity with the specimen.

In addition to the portrayal of macro-etched surfaces, this method of illumination provides an effective means of displaying minute irregularities such as hair-line cracks on polished surfaces.

Exposures required vary within wide limits, being proportional to the square of the aperture number used and also, when photographs on a larger scale than about half actual size are being taken, to the square of the magnification. The intensity of the light thrown by projector lamps depends on their distance and the angular width of the beam they are set to project, whilst the proportion reflected to the camera is dependent also on the nature of the surface of the specimen and its colour.

An exposure meter of the extinction type may be used; this type is held to the eye in a position approximating to that of the camera, and the light from the object to be photographed, which is picked up by it, is reduced by an adjustment until some mark or figure inside the instrument is no longer visible. The use of such a meter is simplified if, after fixing everything in readiness for exposure, a sheet of white card is placed immediately in front of the specimen, and the light reflected from this be measured. Allowance for colour and reflectivity may be made from previously determined data.

Colour Screens.—The etched surfaces of some of the non-ferrous metals show structures in which some grains or areas reflect light which is very non-actinic in colour, and these are apt to show excessive contrast in the photograph unless light is used of a colour similar to that of the darker areas of the specimen.

The definition of lenses of medium and long focus is impaired when colour filters are fitted to them, unless these are mounted in optically worked glass, and a set of such

filters in various colours is an expensive item. Stained gelatin and celluloid filters, cut to fit in between the components of the lens, may be used, but these are fragile and troublesome, and a better method is to make use of a set of tinting screens to fit on to the projector lamps. These may be purchased very cheaply and with them there is no impairment of definition in the lens. Usually, however, colour filters are not required.

Photographic Materials of similar grades to those used for micro-work are suitable, panchromatic emulsions being called for when coloured light is used.

CHAPTER V

THE STRUCTURE OF PURE METALS AND OF ALLOYS

Pure Metals

PURE metals in the cast or annealed condition present under the microscope a system of polygonal grain boundaries representing sections through polyhedral crystal grains which constitute the mass of the metal.

These polyhedral grains, though lacking in external geometrical symmetry, are true crystals the growth of which has suffered interference by contact with similar neighbouring crystal grains. A crystal, the external form of which is defined in this way by its surroundings, is called an allotriomorphic crystal.

The crystal structure of the metals has been shown by X-ray analysis to consist of an orderly geometrical arrangement of the atoms on what is known as a "space lattice." This is a system of points formed by the intersection of three sets of planes parallel to pairs of principal axes of the crystal. The complete pattern consists of repetitions of a group of such points known as the unit cell. The space lattice may be thought of as formed by the corners of the unit cells. Many metals crystallise in the cubic system, and the unit cell is a cube of very minute dimensions. The smallest particle visible at the highest possible magnification under the microscope will be about 1000 times the linear dimensions of the unit cube, its surface will cover about 1,000,000 such cubes. In most of the common metals the atoms are arranged on a face-centred cubic lattice, the unit cell being a cube with one atom at each corner and one at the centre of each of its six faces (Fig. 59). In some metals the atoms are arranged on a

body-centred cubic lattice in which the unit cube has an atom at each corner and one at the centre of the cube (Fig. 60). The more commonly employed metals crystallising in the cubic system are given in the following table, together with the

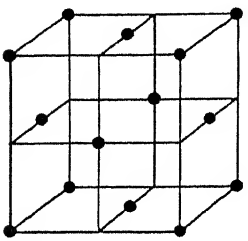


Fig. 59—Face-centred Cubic Lattice.

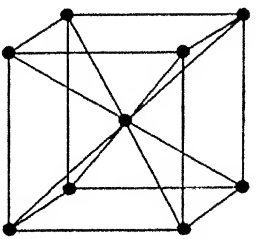


Fig. 60—Body-centred Cubic Lattice.

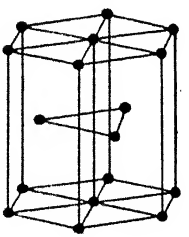


Fig. 61 — Close-packed Hexagonal Lattice.

length of side (or parameter) of the unit cell (a) expressed in Ångstrom units (1 Å. = 10^{-8} cm.).

Face-centred cubic

	Cu.	Ag.	Au.	Al.	Pb.	γ-Fe.	β-Co.	β-Ni.
a =	3·61	4·07	4·07	4·04	4·94	3·63 (at 1100° C.)	3·55	3·52

Body-centred cubic

	V.	Ta.	α-Cr.	Mo.	W.	α-Fe.
a =	3·01	3·30	2·88	3·14	3·16	2·86

Next in order of importance is the close-packed hexagonal structure (Fig. 61), a structure which would be obtained by stacking spheres so that they are in contact with as many neighbours as possible and one which is associated with relatively poor ductility at atmospheric temperature.

Close-packed Hexagonal

	Be.	Mg.	Zn.	Cd.	β-Cr.
a =	2·27	3·20	2·66	2·97	2·72
c =	3·59	5·20	4·94	5·60	4·42

a = length of side of the equilateral triangles of the basal plane.
c = height of unit cell.

There remain only a few common metals with more complicated types of structure.*

* For further data, see "The Structure of Metals and Alloys," by W. Hume-Rothery. Published by the Institute of Metals, 1936.

The formation of crystal grains in metals can be interpreted by analogy with the freezing of other pure liquids, *e.g.* water. During the cooling of a pure liquid, when the freezing point is reached solidification begins (in the absence of super-cooling) at numerous centres. The minute crystals formed increase in size by throwing out branches in certain directions bearing a relation to the symmetry of the crystal. The dendrites thus formed continue to grow at a rate depending on the temperature conditions in their immediate neighbourhood, until their growth is interfered with by meeting neighbouring crystals. In this way the skeleton of the structure and the main outline of the crystal grain boundaries are mapped out. Subsequent solidification takes place by further dendritic growth on a smaller scale in the interstices of the original dendrites, finally resulting in a polyhedral structure such as is shown in Fig. 53. Each polyhedral grain is uniform in composition and internal structure because it is made up of a single constituent, crystallising at a constant temperature.

If such a metal is rolled, hammered or forged, the crystals are broken up, and if the operation is carried out hot they are continuously re-formed. If the rolling is carried out cold the crystals are deformed, but the metal may be made to recrystallise by subsequent annealing.

The effect of annealing will be dealt with more fully later, but here it may be remarked that straining followed by annealing often results in the formation of twin crystals. Neighbouring crystals of the same chemical composition and constitution, but orientated symmetrically about an axis as mirror images of one another, are known as twin crystals. Such crystals have one face in common, the boundaries between the neighbouring crystals appearing in section under the microscope as a straight line (or several parallel lines) across the crystal grain. The presence of such twinned crystals denotes that the metal at some stage in its history has undergone permanent deformation, though the absence of twins is not sufficient evidence of the absence of such treatment. Fig.

54 shows the structure of rolled and annealed copper. It consists of copper grains showing the characteristics of twinned crystals. The dark etching globules are impurities, chiefly oxide.

Nickel, lead and iron also show a simple polyhedral structure (Figs. 55, 56 and 57). As a micro-constituent pure iron is referred to as ferrite. In spite of their similarity of appearance, the history of the formation of ferrite grains is far more complicated than that of the copper grains or those of the other metals illustrated.

If pure copper is allowed to cool from the liquid state the rate of cooling suffers an arrest while solidification takes place at constant temperature, but afterwards the temperature falls without interruption down to that of the surrounding atmosphere. Its other properties, such as its specific volume, also show no discontinuity. Iron, however, behaves quite differently. The melting point of pure iron is 1535° C. and on cooling from the melting point the rate of cooling suffers three definite arrests at about 1403°, 910° and 768° C. respectively. If carbon is present, a fourth arrest occurs at about 700° C., increasing in importance with increase in amount of carbon: this was the first arrest point to be observed and was originally known as A. It is now termed A_1, that at 768° C. being A_2, at 910° C. A_3 and the upper point A_4. The same critical points are also observed on heating, but the actual temperatures are a little higher than those found on cooling. It was therefore necessary to distinguish between the points on the cooling and on the heating curve, and this was done by adding r (*refroidissement*) or c (*chauffage*) to the symbol. Thus Ar_3 indicates the point observed in the neighbourhood of 910° C. in cooling pure iron, Ac_3 represents the corresponding point on the heating curve, and similarly for the other points.

Several metallic and non-metallic elements are known to exhibit at certain temperatures changes of chemical, physical and mechanical properties, accompanied by changes in crystallographic habit and, frequently, by evolution or absorption of

FIG. 53.

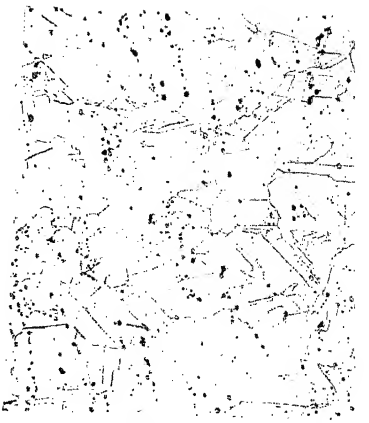


FIG. 54.

FIG. 55.

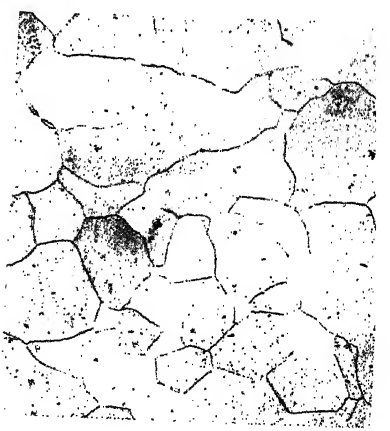
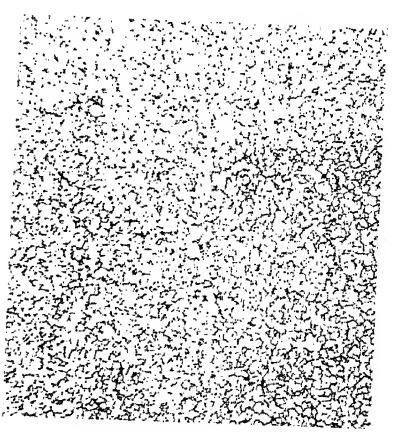


FIG. 56.



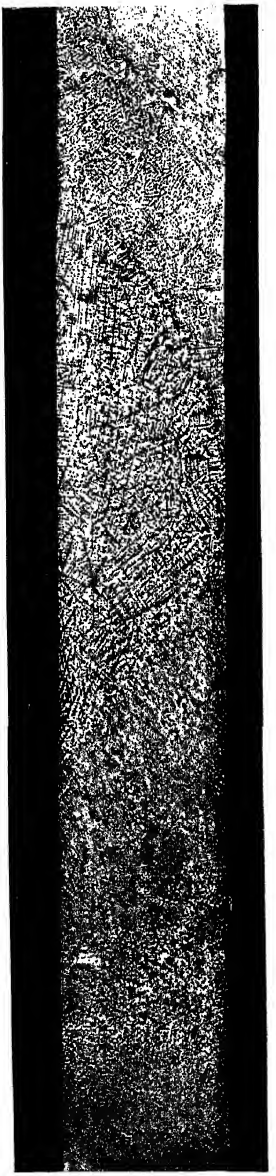


Fig. 49.

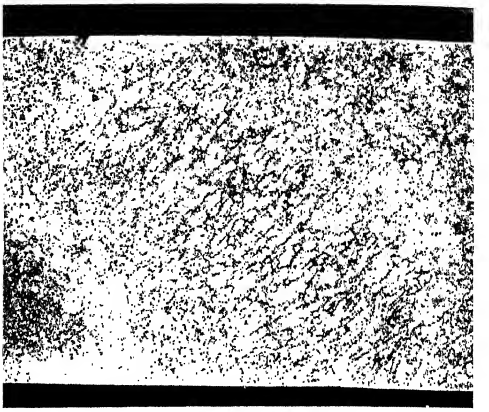


Fig. 50.

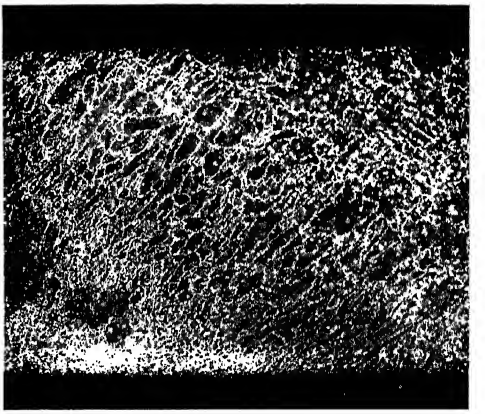
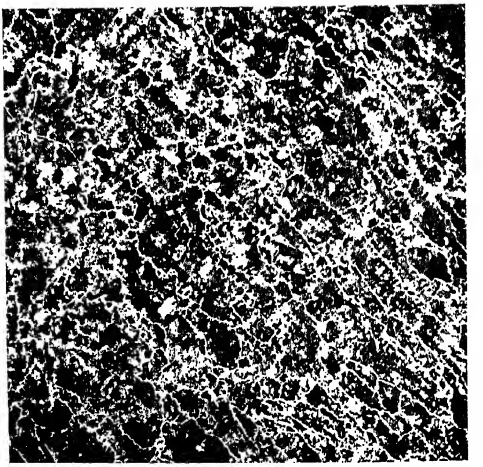


Fig. 51.



heat. In the non-metals oxygen, sulphur and phosphorus, the change is known to depend on a change in the number of atoms in the molecule, and in solids is associated with a re-arrangement of the atoms on a new space lattice. Such changes are referred to as allotropic transformations and the conditions of the element as allotropic modifications.

The absorption or evolution of heat occurring in iron at definite temperatures is considered to be due to allotropic transformations and may be explained by the existence of distinct allotropic modifications of iron. The pure iron which exists at ordinary temperatures is the stable modification at all temperatures up to 910° C. and is known as α-iron, though from 768° to 910° it is non-magnetic and often referred to as β-iron: from 910° to 1403° the metal exists as γ-iron and between 1403° and the melting point δ-iron is stable. All these, however, are not different allotropic modifications of iron. Definite evidence has been obtained by X-ray crystal analysis of a difference in atomic arrangement between α- and γ-iron, while similar evidence has shown that α-, β- and δ-iron are identical in the atomic structure of their crystals.

The thermal changes occurring at the critical temperatures A_2 and A_3 are both accompanied by discontinuities in other physical properties, such as electrical resistance, thermo-electric potential and tenacity. At Ac_2 there is a very sudden fall in the magnetic permeability of α-iron accompanied by no change in the lattice itself. At Ac_3, however, the change in the physical properties mentioned above, as well as in dilatation and specific heat, is accompanied by a change in the cubic lattice from the body-centred type, characteristic of α-iron, to the face-centred type characteristic of γ-iron: and at the Ac_4 point the lattice again reverts to the body-centred type. These changes in lattice structure are accompanied by recrystallisation and refinement of grain size. No refinement occurs on heating through the Ac_2 point, but if iron is heated to Ac_3 recrystallisation occurs, and on cooling rapidly from just above Ac_3 a very fine grain size is obtained (Fig. 58).

Alloys

An alloy may be defined as a mixture with metallic properties composed of two or more elements of which one is a metal. As now understood in industry the name usually implies that an intentional addition has been made to a metal to improve its properties for some particular purpose. The number of phases (p. 3) present together in any solid binary alloy in the state of equilibrium must be either one or two. When the two components of the alloy are metals, these phases are essentially solid solutions, as there is always some degree of mutual solubility, however small it may be, between the two metals. Provided that its homogeneity is not destroyed, the composition of a solid solution may vary within certain limits, and so affect the mechanical properties of the alloy. The single-phase region may be so wide as to extend over the whole range of composition from one metal to the other; or, on the other hand, it may be so restricted as to approximate to a pure metal, or, if intermediate in composition between the two components, to a chemical compound of fixed composition. As the relative proportions of the two metals are progressively altered, the constitution of the resulting alloy may change from a single phase having the structure characteristic of the first metal, to a mixture of two phases, then to the second of these, existing as a single phase and so on, but finishing the series with a single phase conforming to the lattice of the second metal. This series of solid solutions are usually referred to in order by the letters of the Greek alphabet.

In a solid solution formed by small additions to a pure metal, the space lattice is of the type characteristic of the solvent metal, but the points on the lattice are occupied indescriminately by the atoms of the two or more metals present. This type of replacement gives rise to a substitutional solid solution as distinguished from interstitial solid solutions (formed by gases in metals or by carbon in γ-iron) in which

the solute atoms fit into the spaces between those of the solvent.

When zinc is added to copper, the zinc atoms at first replace copper atoms in the face-centred cubic lattice giving the α solid solution. When the limit of this solution is reached, a new phase, the β solid solution, with a body-centred cubic lattice appears. This, in turn, is succeeded by the γ solid solution having a complicated structure, derived from the body-centred cubic, but with a unit cell of 52 atoms. Then follows the ϵ solid solution which has a hexagonal close-packed structure. This succession of phases, face-centred cubic (α), body-centred cubic (β), γ-brass structure (γ) and close-packed hexagonal (ϵ) is characteristic of many alloy systems. Sometimes, as in the copper–silicon alloys, the β-brass structure is replaced by the β-manganese structure, a related cubic structure with 20 atoms in the unit cell.

While these intermediate phases vary in composition between certain limits, they approximate to those which can be represented by the following empirical formulae :—

β.	γ.	ϵ.
$CuZn$	Cu_5Zn_8	$CuZn_3$
Cu_3Al	Cu_9Al_4	—
Cu_5Sn	$Cu_{31}Sn_8$	Cu_3Sn

The copper content of successive phases differs widely from one copper alloy system to another, but the succession of structures is the same ; and the governing factor was observed by Hume-Rothery to be that the ratio of the number of valency electrons to the total number of atoms is constant for each type of phase. For the β structure this ratio is 3 : 2, copper contributing 1 valency electron. For the γ structure, it is always 21 : 13 and for the ϵ-phase 7 : 4. For example, to take the copper–tin series :—

		Electrons.	Atoms.	Ratio.
β .	Cu_5Sn	$5 + 4 = 9$	6	3 : 2
γ .	$Cu_{31}Sn_8$	$31 + 32 = 63$	39	21 : 13
ϵ .	Cu_3Sn	$3 + 4 = 7$	4	7 : 4

The formation of a γ structure when the ratio of valency electrons to atoms reaches 21 : 13 is observed also in ternary

alloys, so that, for example, in the copper–zinc–aluminium alloys, the typical γ structure and properties are obtained if the composition is chosen to keep the ratio of valency electrons to atoms at the value 21 : 13, required by the Hume-Rothery rule. Although only the copper alloys have been specifically referred to, the Hume-Rothery rule that similar phase structures have the same ratio of electrons to atoms is of wide application.

These intermediate phases are sometimes called "Electron compounds," but there is no sharp line of division between them and chemical compounds which obey the ordinary valency laws. An intermediate phase of invariable composition is generally referred to as an intermetallic compound.

So far only the essential character of the microscopical constituents of an alloy has been dealt with. Their structural arrangement (for example the shape and size of grain in a single phase, or the occurrence of two phases in the massive form side by side, or as a eutectic or a dispersion of one in the other) is dependent on conditions of equilibrium between the components at the time of solidification and at various temperatures on cooling, and on the mechanical and heat treatment undergone.

If the lattice structure of two metals is the same and their atomic diameters (or closest distance of approach in crystals of the solid element) very similar, they are often completely miscible in the solid state. As typical of an uninterrupted series of solid solutions, the alloys of copper and nickel may be taken. When a molten copper–nickel alloy is cooled the solid crystallising is neither pure copper nor pure nickel, but a solid solution of the two differing, however, in composition from the liquid. It separates at a temperature lower than the melting point of pure nickel, but higher than that of pure copper, and solidification takes place, not at a constant temperature as for a pure substance, but over a range of temperature. This is indicated by the constitutional diagram constructed from thermal and microscopical data (Fig. 62). Consider, for

example, a solid nickel–copper alloy of uniform composition containing 20 per cent. of nickel and 80 per cent. of copper. If this is melted, fusion begins at 1130° C. and the first drops of liquid formed have the composition represented by the point *b* on the liquidus curve, *i.e.* they are richer in copper than the solid. As the temperature rises, melting continues and is completed at 1180°, the final composition of the liquid (kept uniform by convection and diffusion) being that of the original alloy. On cooling this liquid, solidification begins

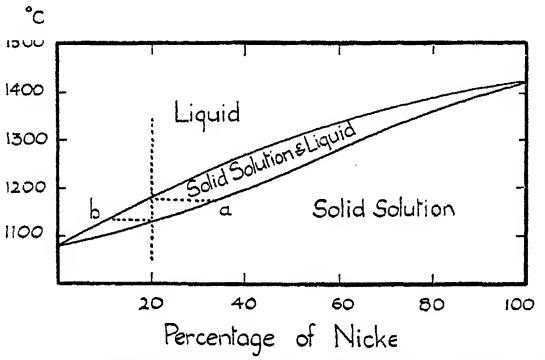


FIG. 62.—Constitutional Diagram of the Copper–Nickel Alloys. (*Guertler and Tammann.*)

The alloys are completely liquid at temperatures above the upper line (the liquidus), and are completely solid at temperatures below the lower line (the solidus).

at 1180°, and the first material to solidify has the composition corresponding to the point *a* on the solidus curve, *i.e.* it is richer in nickel than the liquid. As solidification proceeds, metal progressively poorer in nickel is deposited round the original crystals, that which solidifies last being richest in copper. Hence the structure of the solid cast alloy differs from that of cast copper or nickel, and consists of dendritic crystals originally so-called from their branched tree-like appearance. These vary in composition, being rich in nickel at the centre and rich in copper at the outside, and therefore show a corresponding difference in microscopic appearance at these positions after etching (Fig. 63 and 64).

This lack of homogeneity can be corrected by diffusion if the rate of cooling is sufficiently slow, or if the alloy is

rendered homogeneous by annealing at temperatures below the melting point. The rate of diffusion varies considerably for different metals and the inhomogeneous or "cored" structure persists longest when produced in alloys of those metals which have the slowest rates of diffusion. It is very persistent in nickel alloys. The cored structure of a cast solid solution will be more pronounced the greater the rate of cooling, and will thus be most evident in chill castings. Other conditions being the same, it will be least for alloys in which the range from liquidus to solidus is smallest.

Uniformity of composition of the crystal grains is assisted by mechanical work, *e.g.* rolling, forging, etc., followed by annealing. All the copper–nickel alloys in the rolled and annealed condition have a similar microstructure, that of a homogeneous solid solution (Figs. 65 and 66). When certain etching reagents are used it frequently happens that crystals of identical chemical constitution present different appearances under the microscope, some appearing light and others dark. This is due to a difference in orientation of the crystals, which in some instances may cause a difference in coloration of the grains by the etching reagent, and in others may result in a difference of slope of the etched faces of adjacent grains, some reflecting light back into the microscope tube, and others reflecting it at an angle to the axis of the microscope. By using oblique illumination and rotating the specimen the appearance of any particular grain is then seen to alternate between light and dark according to whether or not the reflected rays travel up the microscope tube. This effect is illustrated by a photograph (Fig. 65) of the structure of Monel metal, and later by other copper alloys.

An example of a series of alloys showing both eutectic mixtures and intermetallic compounds is found in the copper–magnesium alloys. The constitutional diagram of these alloys summarising the data given by cooling curves and microscopical examination is shown in Fig. 77.

The addition of increasing amounts of copper to pure magnesium results in a progressive depression of the freezing point. If a liquid containing 16 per cent. of copper is allowed to cool, magnesium begins to separate at 585° C. and continues to separate as the temperature falls, leaving the liquid progressively richer in copper until the temperature has fallen to 485° C., when the remaining liquid, containing 30·7 per cent. of copper, solidifies at a constant temperature (Fig. 69). Similarly when a liquid containing 37 per cent. of copper is allowed to cool, solidification begins at 512°, but in this instance the solid first separating is the compound Mg_2Cu containing 56·6 per cent. of copper. Thus the liquid this time becomes progressively poorer in copper until the temperature has again fallen to 485° C., when the remaining liquid will have reached the same composition as before, viz. 30·7 per cent. of copper (Fig. 71). This composition, having the lowest melting point, is called the eutectic alloy. An alloy of this composition melts or freezes at a constant temperature and in this respect behaves as a pure substance. Continued separation of either constituent of the eutectic would imply a rise in freezing point of the remaining liquid, a tendency which would be checked by the immediate separation of the other constituent, thus giving rise to the duplex structure which a eutectic shows under the microscope (Fig. 70). A eutectic (not being homogeneous throughout) is not a phase, but a structural constituent. All the copper–magnesium alloys containing 0 to 56·6 per cent. of copper consist of the same two phases magnesium and Mg_2Cu, and the eutectic E_1 is a binary eutectic consisting of these two phases. The magnesium phase contains about 0·03 per cent. of copper.

On passing to the copper-rich alloys of the series, it will be noted that the freezing point of pure copper is progressively lowered by the addition of increasing amounts of magnesium. An alloy containing 93·7 per cent. of copper begins to freeze at 858° C., but the solid separating is not pure copper; it is

FIG. 63.—Cast cupro-nickel (50 per cent. copper : 50 per cent. nickel, used for remelting in the manufacture of nickel alloys), showing grains of copper–nickel solid solution partly surrounded by solid solution richer in copper.

Etched with acid ferric chloride solution. × 50.

FIG. 64.—Chill cast Monel metal. Composition :—Nickel about 70 per cent., copper about 27 per cent. with appreciable amounts of iron and manganese.

It consists of dendritic crystals of the copper–nickel solid solution which solidified first : as solidification proceeded the remaining liquid became richer in copper and finally solidified forming the dark etching inter-dendritic material.

Etched with acid ferric chloride solution. × 100.

FIG. 65.—Monel metal, rolled and annealed at 900° C., consisting of polyhedral grains of a single solid solution, sometimes showing twinning. The difference in shade of the grains is partly due to the formation of a film or patina on some of the crystals, and is partly an optical effect due to different orientation of the rather deeply etched faces of the grains with respect to the axis of the microscope.

Etched with acid ferric chloride solution. × 100.

FIG. 66.—Monel metal, rolled and annealed at 900° C. A clearer and more uniform etch obtained with a 2 : 1 : 1 mixture of nitric acid, acetic acid and water. × 100.

Temper-hardening of a quenched alloy.

FIG. 67.—A hot-rolled nickel–aluminium–copper alloy (copper 87·5 per cent., aluminium 7 per cent., nickel 5·5 per cent.), quickly cooled from 900° C. It consists of polyhedral grains of a single solid solution, showing twinning.

Etched with acid ferric chloride solution. × 100.

FIG. 68.—The same alloy, quickly cooled from 900° C., reheated to 700° C. for three hours and cooled in air, showing precipitation of a second constituent throughout the solid solution with consequent increase in hardness.

Etched with acid ferric chloride solution. × 500

Effect of temper-hardening on the mechanical properties.

	Fig. 67.	Fig. 68.
Yield point, tons per sq. inch .	8·6	22·7
Maximum load, tons per sq. inch	29·2	43·2
Elongation per cent. on 2 ins. .	73	26
Impact figure, ft.-lbs. (Charpy machine, B.S.I. test-piece) .	150	48

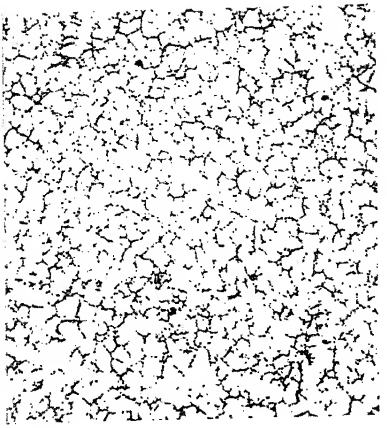
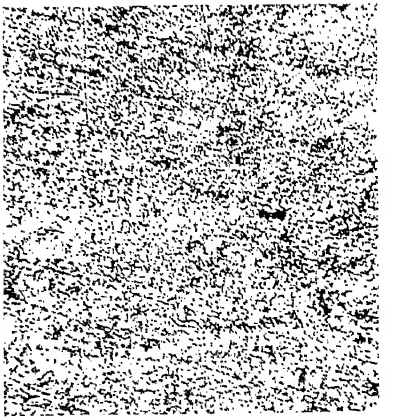


FIG. 63.

FIG. 64.

FIG. 65.

FIG. 66.



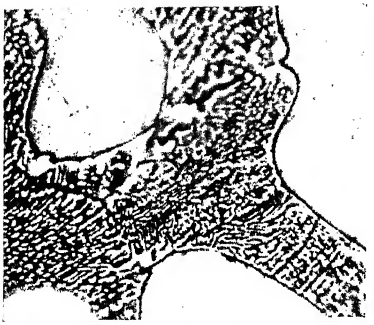


Fig. 69.

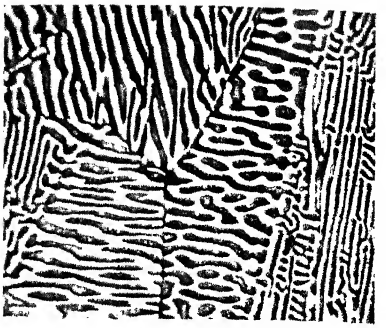


Fig. 70.

Fig. 71.

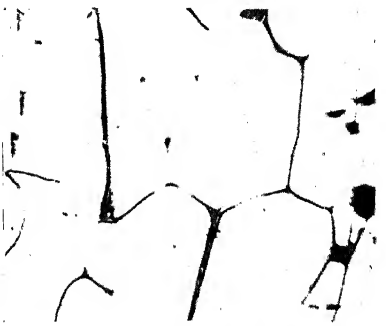


Fig. 72.

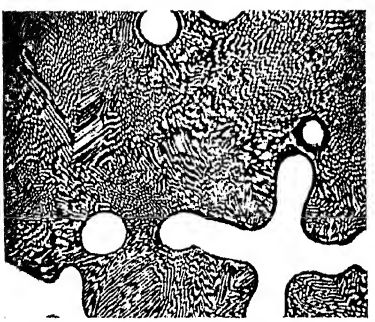


Fig. 73.

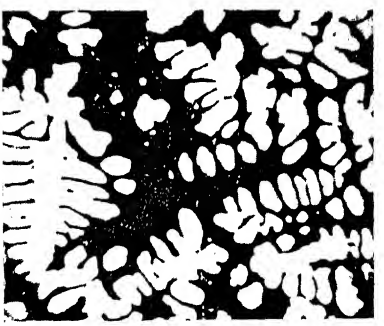
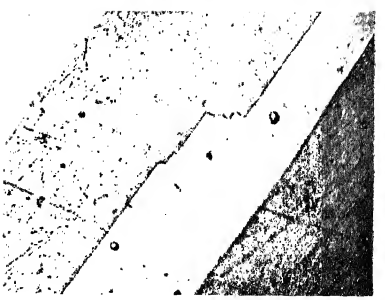


Fig. 74.



Etched with nitric acid in alcohol of concentration 0·5 per cent. for the magnesium-rich alloys and 2 per cent. for the copper-rich alloys.

FIG. 69.—16 per cent. copper. Dendritic crystals of magnesium surrounded by the eutectic of Mg and Mg_2Cu. × 250.

FIG. 70.—30·7 per cent. copper. The alloy consists entirely of the eutectic of Mg and Mg_2Cu. × 250.

FIG. 71.—37 per cent. copper. Plate-like crystals of the compound Mg_2Cu embedded in the eutectic of Mg and Mg_2Cu. × 50.

FIG. 72.—52·4 per cent. copper. Large grains of the compound Mg_2Cu (containing 56·6 per cent. copper) surrounded by a small amount of the eutectic of Mg and Mg_2Cu. × 50.

FIG. 73.—92 per cent. copper. Dendrites of solid solution of magnesium in copper surrounded by the eutectic of this solid solution and $MgCu_2$. × 250.

FIG. 74.—93·7 per cent. copper. Similar to Fig. 73. × 50.

The structures shown in Figs. 69 to 74 are those of the alloys as cast and slowly cooled.

FIG. 75.—97·5 per cent. copper, 2·5 per cent. magnesium. Chill cast ingot, consisting mainly of solid solution of magnesium in copper with a small amount of the eutectic of this solid solution and $MgCu_2$. × 250.

FIG. 76.—The same material as shown in Fig. 75 after being heated at 680° C. for 72 hours and quenched in water. It now consists entirely of solid solution. × 250.

a solid solution of magnesium in copper containing 1·6 per cent. of magnesium which may be referred to as the α solution. As the temperature falls α continues to separate, but its magnesium content increases until at just above 722° C. (provided that cooling has been slow enough for equilibrium to have been maintained) α solid solution containing 2·6 per cent. of magnesium exists in contact with liquid containing 9·7 per cent. of magnesium in the ratio 3·4 : 3·7 (approximately 1 : 1). On reaching 722° C. all the remaining liquid solidifies without further change of temperature, forming a eutectic groundmass in which the crystals first formed from the liquid, or primary crystals, are embedded (Fig. 74). The structure of this eutectic in an alloy containing 8 per cent. magnesium is shown in Fig. 73. The alloy containing 9·7 per cent. of magnesium consists wholly of the eutectic of α and $MgCu_2$: it freezes without change of composition at the constant temperature 722° C.

At the eutectic temperature copper will retain 2·6 per cent. of magnesium in solid solution (Fig. 78). An alloy containing less than this amount of magnesium should therefore consist of uniform polyhedral grains of a single constituent. If, however, cooling is sufficiently rapid, the liquid remaining after the primary separation of very nearly pure copper is sufficiently enriched in magnesium to form some eutectic. The cast alloy therefore shows solid solution and eutectic (Fig. 75), though after long annealing to enable diffusion to equalise the composition throughout, it attains its condition of true equilibrium at the annealing temperature and consists of uniform solid solution (Fig. 76).

In the complete series of copper–magnesium alloys there exist two alloys (containing 56·6 and 83·9 per cent. of copper respectively), which show higher freezing points than neighbouring alloys with slightly more or less copper. If the copper and magnesium contents of the alloys are divided by the atomic weights of these elements (63·6 and 24·3 respectively) it will be seen that the ratio of atoms of magnesium

to atoms of copper in the alloys is 2 : 1 and 1 : 2. These alloys are the chemical compounds Mg_2Cu and $MgCu_2$; they solidify at a constant temperature to form homogeneous solids and their freezing points are depressed by the addition of either copper or magnesium. They thus behave as pure

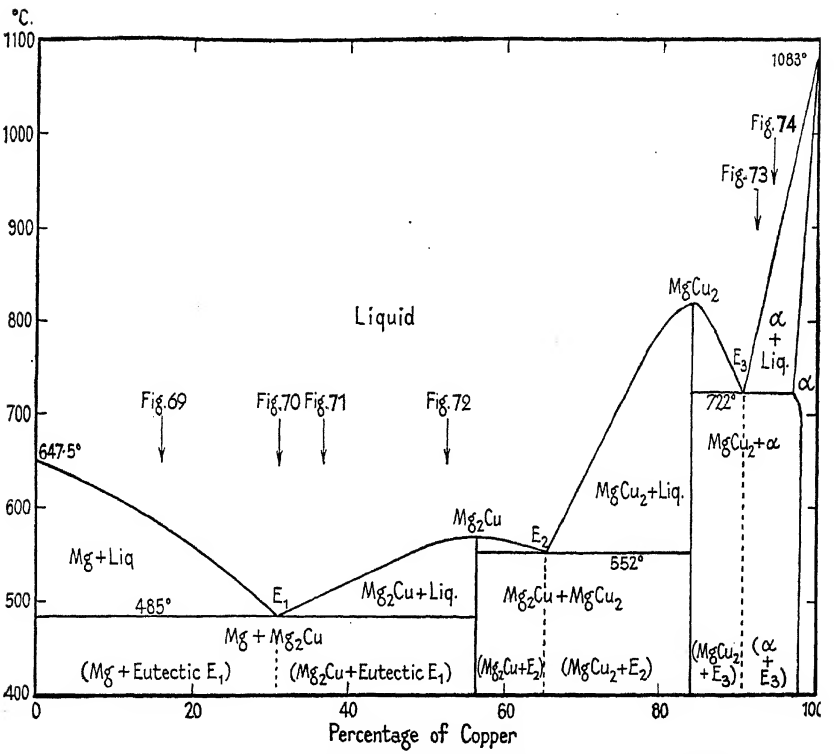


FIG. 77.—Constitutional Diagram of the Magnesium–Copper Alloys. (*Jones.*)

substances. The compound Mg_2Cu together with a little of the eutectic E_1 is shown in the alloy containing 52·4 per cent. of copper (Fig. 72). The complete copper–magnesium system can be split up into three simpler systems: alloys with more magnesium than Mg_2Cu can be regarded as alloys of Mg and Mg_2Cu, those with more copper than $MgCu_2$ as alloys of copper with $MgCu_2$, while the two compounds themselves form a system showing a eutectic Mg_2Cu–$MgCu_2$

melting at 552° C. and containing 32·2 per cent. of Mg_2Cu (or 65·4 per cent. of copper).

Some intermetallic compounds separate from the liquid at temperatures not merely higher than the freezing points of alloys of adjacent composition, but higher than the freezing points of either of the component metals. For example, tin freezes at 232° C. and magnesium at 650° C., but the liquid containing 71 per cent. of tin solidifies completely at about 780° C. to form a homogeneous solid, the compound Mg_2Sn. The freezing points of aluminium and of nickel are respectively 660° and 1450° C., but the alloy containing 68 per cent. of nickel has the highest freezing point of any of the series, viz. 1645° C., and consists of the chemical compound NiAl. Such alloys are not of any industrial utility, but are sometimes a source of trouble. Thus, in making a "hardener" for the introduction of nickel into aluminium alloys, the nickel content is limited in practice to about 20 per cent. on account of the very high melting point of alloys containing more than that amount. Furthermore, nickel must always be slowly added to molten aluminium, for if aluminium is added to nickel, or if a large amount of undissolved nickel is present, the composition of the alloy will, at some stage before melting and mixing is complete, pass through the range in which NiAl is formed and the whole mass will set to a relatively infusible solid.

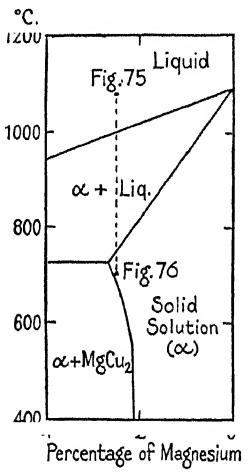


FIG. 78.—Part of the Constitutional Diagram (Fig. 77) indicating the Solid Solubility of Magnesium in Copper. (*Jones.*)

Chemical compounds which occur in the free state in alloys are very hard and brittle substances. When they form a constituent of industrial alloys they are usually present only in small amounts. In many cases the compound has the property of entering into solid solution with one or both of

the components of the system: in other cases it may possess a limited range of stability and only appear in the solid alloy at temperatures considerably below the melting point.

Supersaturated Solid Solutions

A sloping line in the constitutional diagram indicates that the mutual solubility of two phases is progressively changing with change of temperature. Liquid solutions of salts in water usually, but not invariably, show increasing solubility as the temperature is raised, and if the solution is cooled in such a way as to avoid the separation of the solid substance a supersaturated liquid solution is obtained at atmospheric temperature, and by suitable means the excess of dissolved substance may be precipitated or made to crystallise out. Similarly in many alloy systems the limit of saturation of a solid solution decreases with fall of temperature. These solid solutions may often be retained in the supersaturated condition at atmospheric temperature by quenching. Thus a copper-rich supersaturated solid solution can be obtained in certain nickel–aluminium–copper and manganese–aluminium–copper alloys, but not in aluminium–copper alloys, since the solid solubility of aluminium in copper increases as the temperature falls, whilst its solubility in the alloys containing nickel or manganese decreases. The structure of a nickel–aluminium–copper solid solution is shown in Fig. 67. If this alloy is reheated after it has been quenched or if it is slowly cooled instead of being quenched, separation of the excess of the dissolved constituent occurs (Fig. 68), and the slower the rate of cooling the larger are the separated particles. The effect of this separation of small particles within the original grains of the solid solution is to increase its hardness, and for this reason the process is sometimes known as "precipitation hardening."

The deformation which occurs in a metal or alloy under stress is due to minute movements occurring under shearing stress on the plane surfaces of slip in the crystal grains.

Anything which will act as an obstruction to the process of slip will thus raise the stress required to produce a given deformation. In this way separated particles of the dissolved constituent dispersed throughout the crystals will cause an increase in hardness. In general, fine particles cause greater hardening than coarse particles. To obtain the greatest effect the precipitated particles must be of such a size and distribution as to produce maximum interference with the process of slip within the crystal. In other words, the hardening depends on the degree of dispersion of the particles, and is accordingly sometimes known as "dispersion hardening." The lower the temperature at which the solid solution can be induced to break down, the finer will be the particles deposited.

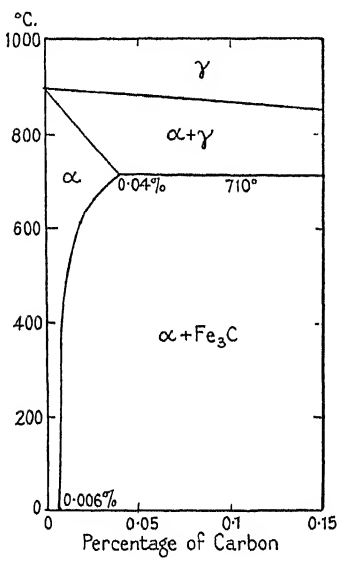


FIG. 79.—Constitutional Diagram indicating Solubility of Carbon in α-Iron. (*Köster.*)

Treatment which consists of rest at atmospheric temperature after quenching is known as "ageing" and the effect as "age-hardening." If reheating is necessary to induce precipitation, the treatment is sometimes known as "artificial ageing," but might preferably be referred to as tempering, the effect produced being "temper-hardening."

This type of hardening is of wide occurrence and was first observed, long before its true character was understood, in the aluminium alloy, Duralumin. It is shown by both ferrous and non-ferrous alloys. Thus carbon can give rise to marked age-hardening in very mild steel quenched from 700° C. The solubility of carbon in α-iron is probably about 0·006 per cent. at atmospheric temperature and 0·04 per cent. at 700° C. (Fig. 79). In a 0·1 per cent. carbon steel, quenched

from 700° C. and aged for a month at atmospheric temperature, the elastic limit, tensile strength and hardness may be increased by at least 50 per cent. and the elongation halved, owing to the precipitation of finely divided carbide (not visible under the microscope) from the supersaturated solid solution. The solubility of nitrogen in iron is 0·5 per cent. at 580° C. and only about 0·01 per cent. at atmospheric temperature, and the age-hardening effect of nitride reinforces that of carbide, especially in Bessemer steels. In these

LIMITS OF SOLID SOLUBILITY AT ATMOSPHERIC AND AT RAISED TEMPERATURES

Solvent metal.	Composition of precipitated particles.	Limits of solid solubility.	Authority.
Iron	Fe_3C	0·04% C at 715° C. : 0·006% at 20° C.	Köster.
	Fe_4N	0·5% N at 580° C. : 0·015% at 20° C.	Fry and Epstein.
	Fe_3P	2·8% P at 1050° C. : 1·1% at 745° C.	Vogel: Haughton.
	Fe_2Mo_2	24% Mo at 1440° C. : 6·0% at 20° C.	Sykes.
	Fe_2W_2	33% W at 1525° C. : 8·0% at 20° C.	Sykes.
	(Cu)	2·4% Cu at 810° C. : 0·4% below 600° C.	Buchholtz and Köster.
Copper	γ(Si, Cu)	6·7% Si at 726° C. :<4·0% at 300° C.	Smith.
	(Ag)	8·2% Ag at 750° C. : 0·7% at 400° C.	Stockdale.
Silver	(Cu)	8·8% Cu at 780° C. : 1% at 200° C.	Stockdale.
Lead	(Sb)	2·45% Sb at 247° C. : 0·25% at 20° C.	Dean.
	(Sn)	16% Sn at 175° C. : 2·0% at 25° C.	Morgan and Roberts.
	(Bi)	40% Bi at 125° C. : 18·0% at 20° C.	Herold.
	Pb_3Ca	0·1% Ca at 325° C. : 0·01% at 75° C.	Schumacher and Bouton.
Aluminium	(Si)	1·65% Si at 577° C. : 0·05% at 200° C.	Dix and Heath.
	$CuAl_2$	5·6% Cu at 548° C. : 0·5% at 200° C.	Dix and Richardson.
	Mg_2Si	1·85% Mg_2Si at 595° C. : 0·2% at 200° C.	Dix, Keller and Graham.
	Mg_2Al_3	14·9% Mg at 451° C. : 4·0% at 200° C.	Dix and Keller.
	$MnAl_3$	0·65% Mn at 657° C. : 0·13% at 450° C.	Dix and Heath: Stockdale.
Magnesium	Al_2Mg_3	12% Al at 436° C. : 6% at 20° C.	Saldau and Zamotorin.
	ZnMg	6% Zn at 340° C. : 2% at 100° C.	Chadwick.

instances the hardness is not increased so much if the temperature is raised above atmospheric. In other iron alloys, *e.g.* copper–iron, molybdenum–iron, tempering is essential if any effect is to be obtained; precipitation will not occur at atmospheric temperature. In the age-hardening which occurs at atmospheric or slightly raised temperatures (*e.g.* that of Duralumin, p. 246) it is possible to distinguish at least three distinct processes, nucleus formation, ultra-microscopic precipitation and coalescence, of which the first contributes the greatest hardening effect. In alloys which have to be heated to a fairly high temperature to initiate hardening these stages follow one another so rapidly that a simple precipitation theory is sufficient to account for the observed behaviour.

Moreover in practice, in such materials as copper steels coalescence and microscopically visible precipitation are essential if undue brittleness is to be avoided.

The importance of a diminution of solid solubility with fall of temperature as a basis of heat treatment of ferrous and non-ferrous alloys is being increasingly recognised. Some of the principal alloys in which it has been observed are given in the table on page 91.

The Peritectic Transformation in Iron–Carbon Alloys and the Identity of α- and δ-Iron

Reference has been made to the allotropic form of pure iron existing between 1403° C. and the melting point, and

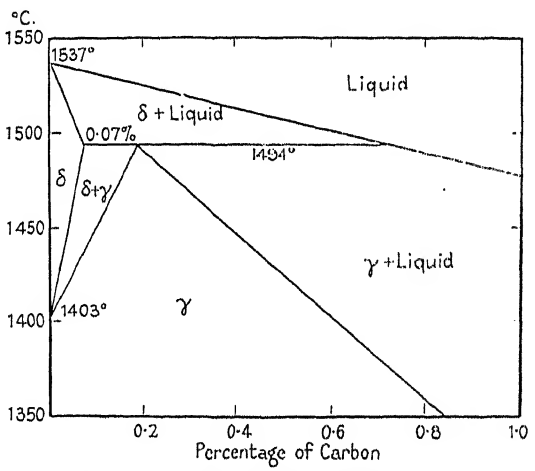


FIG. 80.—The δ-Region of the Iron–Carbon Diagram. (*Andrew and Binnie.*)

known as δ-iron. The temperature range in which it is stable is greatly affected by the presence of other elements, and is rapidly narrowed by the addition of carbon, until it ceases to be present in iron–carbon alloys when the carbon reaches 0·2 per cent.

The diagram showing the region of stability of the solid solution of carbon in δ-iron is given in Fig. 80. The temperature at which the absorption of heat (Ar_4) occurs on

cooling rises with increase in carbon content until it reaches 1494° C. and then remains constant. The δ-iron which separates from the liquid steel cannot hold more than 0·07 per cent. of carbon in solid solution: if the steel contains between 0·07 and 0·7 per cent. of carbon solidification is completed at 1494° C. by a change in which two phases, δ and liquid, react to form a single phase γ. This type of change is known as a peritectic transformation. In an alloy having the composition and temperature represented by the peritectic point (0·2 per cent. carbon, 1494° C.) three phases, liquid, δ and γ, may exist together in equilibrium; just as three phases may exist together in equilibrium at a eutectic point, for example magnesium, Mg_2Cu and liquid at the eutectic E_1 in Fig. 77. With change either of temperature or of composition one, at least, of the three phases must disappear. If the diagram is viewed upside down, the analogy between the peritectic and eutectic points may be seen, the former occurring at a maximum temperature in the series of alloys and the latter at the minimum.

The process of solidification of liquid steel containing 0·14 per cent. of carbon may now be followed. At its freezing point it begins to deposit crystals of δ-iron. At 1495° C. it consists of δ and liquid in the ratio (0·7–0·14) : (0·14–0·07) or 8 : 1. At the peritectic temperature much of the δ will transform to γ absorbing the carbon necessary to attain the composition 0·2 per cent., from the remaining carbon-rich liquid: so that on complete solidification (if equilibrium has been maintained) the steel contains δ and γ in the ratio (0·2–0·14) : (0·14–0·07) or approximately 1 : 1. As cooling continues the amount of δ solid solution diminishes until the alloy consists of the γ solid solution only.

It will be clear that much of the peritectic reaction occurs in the solid δ which has already separated, and that with fairly rapid cooling there may not be an opportunity for attaining complete equilibrium. The peritectic change may have considerable importance in questions relating to the

structure of ingots and castings but its influence has not yet been fully investigated.

In the practical heat treatment of carbon steel the A_4 transformation is too remote from the temperatures normally used to be of consequence, and δ-iron is only of importance because of its identity with α-iron. It might, with advantage,

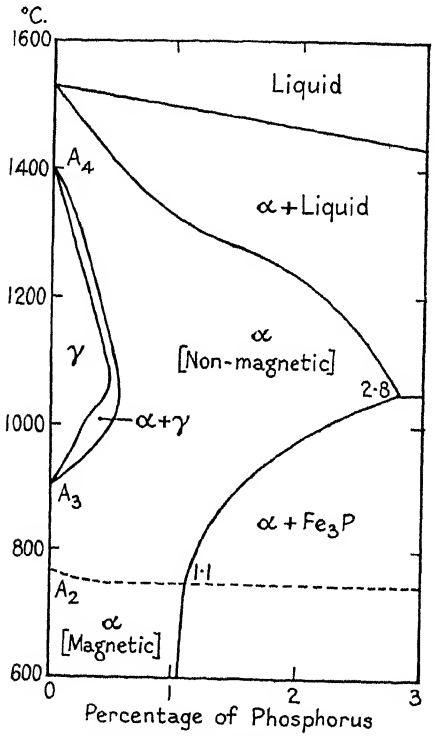


FIG. 81.—The γ-Loop of the Iron–Phosphorus Diagram. (*Haughton.*)

be more generally referred to not as δ-, but as α-iron. The fact that α- and δ-iron are shown by X-ray crystal analysis to possess the same structure received a complete explanation when the addition of certain elements to pure iron came to be studied. It has been found, for example, that the addition of silicon to iron progressively raises the A_3 point and lowers the A_4 point, thus narrowing the range of temperature within which γ-iron can exist, until, in the presence of 2 per cent. of

silicon, its region of stability is reduced to a few degrees and with a little more silicon it cannot exist at all. The stable condition below A_3 merges into that above A_4, and the alloy consists of α-iron (with silicon in solid solution) at all temperatures between atmospheric and the melting point. The following are some of the elements which have a similar effect in their alloys with iron, the percentage given being approximately that at which the γ phase ceases to have any range of stability, and α remains the sole constituent right up to the melting point (Fig. 81).

Element.	Al.	Si.	P.	V.	Cr.	Mo.	W.
Percentage	1·0	2·2	0·55	1·2	11·6	3·0	6·0

In alloys containing less than the percentages given above, the conversion of α to γ may not be complete, as the γ-loop is bounded by a region (varying in width in different systems) in which both phases exist together in equilibrium. These figures refer to the pure binary alloys; the presence of carbon, manganese, nickel and some other elements extends the region in which the γ phase is stable in these alloys.

If iron is heated to a temperature just above Ac_3 recrystallisation occurs with refinement of grain size, but in the presence of elements which eliminate the change from α to γ no such refinement is possible. The α-iron crystals continue to increase in size with increasing temperature. This fact is of great importance in considering the effect of heat treatment on the properties of alloys of iron containing large amounts of the elements referred to above.

CHAPTER VI

THE STRUCTURE AND PROPERTIES OF INGOT IRON AND WROUGHT IRON

THE purest forms of iron, as already mentioned, consist entirely of ferrite (Figs. 10 and 57). Certain impurities may be present in small amount in the iron without the formation of another constituent in the microstructure: they are retained in solid solution in the ferrite. Such, for example, are phosphorus, manganese and silicon. Carbon, however, even in small amounts separates in a manner which will be described in the next chapter.

Hence malleable or wrought iron, which in its purest forms contains very little carbon (say 0·05 per cent.), consists essentially of ferrite but the properties of this micro-constituent are profoundly influenced not only by impurities in solution, but by the presence of slag (silicates and oxides) which is characteristic of wrought iron. This slag is the most marked micrographical distinction between wrought iron produced in the pasty condition (puddling process) and ingot iron or dead mild steel produced in the liquid state. As the puddled iron is rolled these masses of slag become elongated, and then have an important effect on the properties of the metal. The slag occurs in pencils drawn out in the direction of rolling and visible in the transverse section as round greyish dots, but in the longitudinal sections as streaks; while the mass of metal consists of irregular grains of ferrite, which although deformed in rolling are no longer elongated, because the temperature at which the rolling has been done was sufficiently high to permit the ferrite crystals to re-form.

Of commercial wrought irons, Swedish Bar Iron is most free from slag inclusions (Figs. 83, 84). The best brands of

English malleable iron, best Yorkshire iron (*e.g.* Lowmoor iron, Figs. 85, 86), show a similar microstructure, but as a rule contain more slag. Staffordshire irons (Fig. 87) contain even larger amounts of slag, and their structure is also often modified by the presence of a certain amount of carbon forming the constituent pearlite which is met with in steels.

The tensile strength of ingot iron or dead mild steel is 19 to 23 tons per sq. in., with an elongation of 40 per cent. or more, on 2 in.; wrought iron has a tensile strength of 22 to 26 tons per sq. in., with an elongation of about 30 to 40 per cent. on a 2-in. test-piece. The strength of a wrought-iron plate is greater along the grain (*i.e.* in the direction of the rolling) than across the grain, and this difference is more pronounced the further the rolling is carried. It may be bent double without fracture either hot or cold, and if of good quality is very tough. Here again the effect of the grain is evident, for it is far more resistant to bending about an axis perpendicular to the grain than about one parallel to that direction.

If a bar of wrought iron is nicked with a file and then bent by hammering, it should break with a fibrous fracture. The "fibres" are not merely the slag streaks—these can often be distinguished in the fracture by means of a lens—but they are grains of pure iron, elongated by bending, in which the slag is embedded. The ferrite of a good tough specimen of wrought iron normally undergoes extensive deformation before fracture. If the iron is broken by a sudden blow, the fracture may be complete before there has been time for such elongation, and a "crystalline" fracture results. An excessively coarse grain size due to overheating (p. 114), or the presence of too much phosphorus or sulphur, causes iron to break with a crystalline fracture and low elongation, even when slag fibres are present to interrupt the path of the fracture.

The chief impurities present in wrought iron are:—

Carbon.—This is usually under 0·15 per cent., but may rise to 0·25 per cent. In this case the tensile strength is raised

and the elongation diminished. The metal begins to resemble steel, and shows signs of hardening on quenching in water from a red-heat. The presence of carbon (as carbide of iron) is revealed by the microscope (Chapter VII).

Sulphur is not often present, in excessive amounts, but it may be injurious even in small quantities. Some will be contained in the slag, but if it occurs in the metal as sulphide of iron (the manganese content being very low) it renders the iron brittle both when hot and when cold.

Silicon is always present, partly in the slag and partly dissolved in the ferrite as silicide of iron, and so unrecognised under the microscope. A figure above which the total silicon becomes injurious cannot be laid down, the dissolved silicon having a far greater effect than that occurring in the slag as silicate of iron.

Phosphorus is always present, and here again its action depends on its distribution between slag and iron in which it occurs as phosphide, Fe_3P, dissolved in the ferrite, rendering the metal brittle.

Uneven distribution of phosphorus or of silicon in the iron may result in the presence throughout the bar of streaks of metal containing a sufficiently high content of these elements to eliminate the α to γ change on heating. Hence, when the metal is annealed, excessive grain growth occurs in place of the usual refinement, thus giving rise to defective layers of so-called "burnt iron." *

Practical Notes

Polishing.—The usual method, finishing off with diamantine, wet.

Transverse and longitudinal sections should be examined.

The polished surface of a longitudinal section often shows slag streaks, visible to the naked eye.

Etching.—A 5 per cent. solution of nitric acid in alcohol

* H. J. Gough and A. J. Murphy: "Defective Laminations in Wrought-iron," *Journal of the Iron and Steel Institute*, 1931 (1), vol. cxxiii, p. 285.

or a saturated solution of picric acid in alcohol. Time required $\frac{1}{2}$ to 1 minute.

Longer treatment with weaker solutions of nitric acid often results in coloration of the grains. The coloration alters with time and strength of acid, owing to the more rapid formation or subsequent dissolution of an oxide film on the surface of the grains. It is influenced by the impurities present in solid solution, *e.g.* phosphide or silicide of iron.

Reagents for detecting the distribution of phosphorus are referred to on page 180.

It is often difficult to obtain ferrite grains in wrought iron free from minute black specks or pits. These may be due to tiny slag or oxide spots, but they are more frequently caused by imperfect polishing or too violent an etching agent. Etching proceeds more slowly but more regularly in alcoholic than in aqueous solutions.

If a section of iron is deeply etched with nitric acid or with a 10 per cent. solution of cupric ammonium chloride in water, pits are formed in the ferrite, and often show a geometrical pattern illustrating the truly crystalline symmetry of the polyhedral grains.

CHAPTER VII

THE STRUCTURE AND PROPERTIES OF NORMALISED AND ANNEALED CARBON STEELS, AND THE EFFECT OF HOT- AND COLD-WORK

THE addition of carbon to iron results in the most remarkable and valuable series of alloys known; and in the study of steel and cast iron and of the complex changes they undergo through variation of composition and of heat treatment, the iron–carbon equilibrium or constitutional diagram will serve as a guide to the correct interpretation of the microstructures observed. An equilibrium diagram deals only with stable phases in equilibrium, and nearly all the constituents of hardened steel are in this sense unstable, though their tendency to revert to equilibrium conditions is inappreciable at atmospheric temperature. Such a diagram is further limited to equilibrium between pure components; and the influence of impurities or of special elements in steel is not indicated by the iron–carbon diagram. Nevertheless the constitutional diagram provides a basis on which all the micro-constituents of steel may be classified and for practical purposes furnishes a temperature chart which summarises in a broad and general way the effect of heat treatment on the structural constituents, and through these on the mechanical properties of the steel.

The complete diagram up to 5 per cent. of carbon is included later (Fig. 220): the portion which concerns steels below 1000° C. is given in Fig. 82.

It may be useful to trace in this diagram the changes which occur on cooling pure carbon steels of varying carbon content from temperatures above the upper limit of the critical range, at which the steel consists of a solid solution of carbide at

iron (or carbon) in γ-iron. For this reason more weight is given in Fig. 82 to the position of the critical points on cooling, which are often 30 or 40 degrees below those obtained on heating.

Cooling of a 0·3 per cent. Carbon Steel.—On reaching a temperature of about 804° C. the uniform rate of cooling suffers an arrest (Ar_3), since heat begins to be evolved while the solid solution deposits α-iron in the non-magnetic (β)

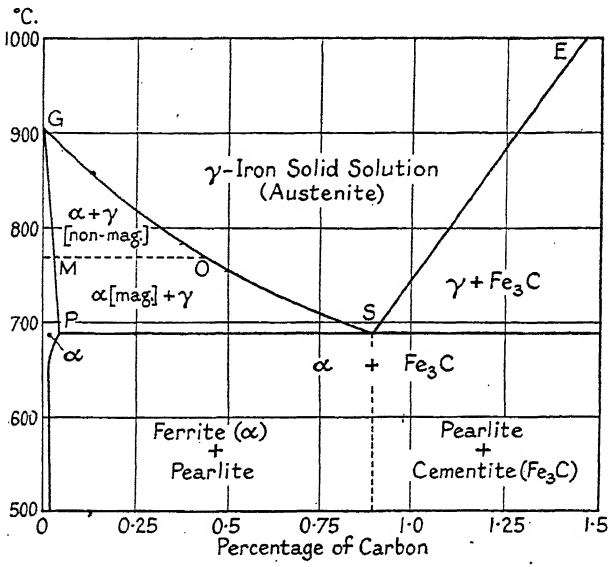


FIG. 82.—Part of the Iron–carbon Constitutional Diagram. For solid solubility of carbon in α-iron, see Fig. 79.

condition. The first separation of ferrite takes place in the grain boundaries of the γ-iron solid solution, and a network develops by gradual deposition of the ferrite at the boundaries of each grain. The solid solution remaining enclosed in the network becomes richer in carbon, and as the temperature falls more ferrite is deposited, the solid solution at any temperature always containing a limiting amount of carbon represented by points on the line GOS. On reaching 768° C. a second arrest (Ar_2) occurs, associated with the change of the α-iron from the non-magnetic to the magnetic condition.

All etched with nitric acid solutions. Magnification 250 diameters.

FIGS. 83 to 87.—Wrought iron, consisting of grains of ferrite and slag.

FIG. 83.—Swedish bar iron, longitudinal section, showing streaks of slag cutting through ferrite grains.

FIG. 84.—Swedish bar iron, transverse section, showing slag dots, *i.e.* sections across pencils of slag.

FIG. 85.—Lowmoor iron, longitudinal section. Rather deeply etched—slag corroded, and ferrite grains tinted.

FIG. 86.—Lowmoor iron, transverse section. Etched with stronger acid. The slag dots have been corroded, giving in many cases pits of geometrical outline.

FIG. 87.—Best Staffordshire iron, transverse section. Slag more plentiful than in the other brands shown.

FIG. 88.—Dead mild steel, carbon 0·09 per cent., after deformation by an explosive charge. The ferrite grains show Neumann bands.

In this connection see F. B. Foley and S. P. Howell, "Neumann bands as evidence of the action of explosives upon metal," *Transactions of the American Institute of Mining and Metallurgical Engineers*, Sept. 1922.

Neumann bands are probably regions of severely disturbed orientation, rather than narrow twin crystals as at one time supposed: see W. Rosenhain and J. McMinn, "The Plastic Deformation of Iron and the Formation of Neumann Lines," *Proc. Roy. Soc.*, A., vol. cviii, pp. 231–239.

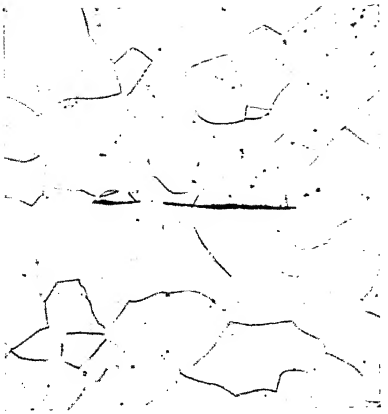


FIG. 83.

FIG. 84.

FIG. 85.

FIG. 86.

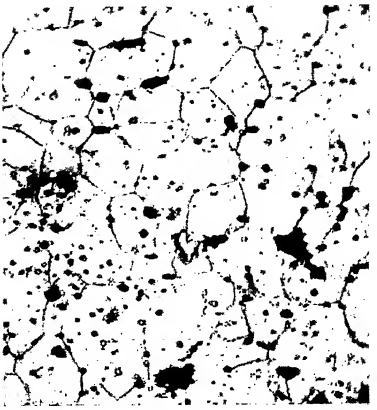


FIG. 87.

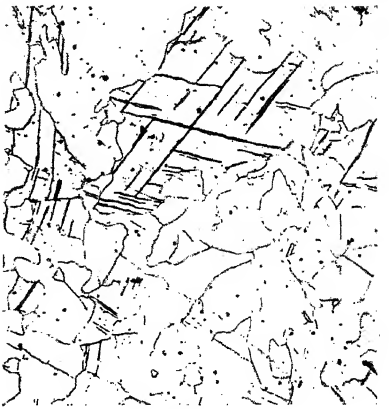


FIG. 88.

FIG. 89.

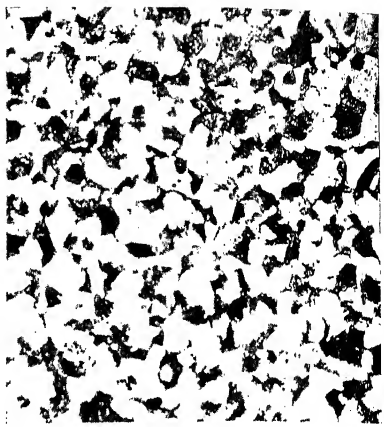


FIG. 90.

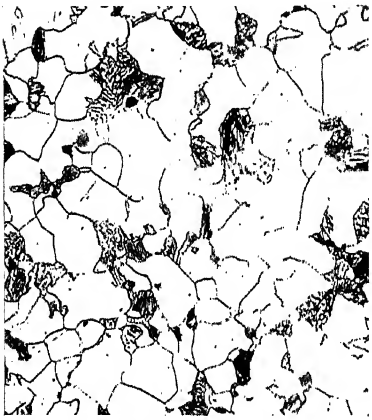


FIG. 91.

FIG. 92.

FIG. 93.

FIG. 94.

Normalised and annealed carbon steels.

All etched with 1 per cent. nitric acid in alcohol. Magnification 100 diameters.

FIG. 89.—	Carbon	0·15	per cent.	Normalised.
,, 90.—	,,	0·3	,,	,,
,, 91.—	,,	0·3	,,	Annealed.
,, 92.—	,,	0·45	,,	Normalised.
,, 93.—	,,	0·6	,,	,,
94.—		0·9		

The light-etching constituent decreasing in amount with increase of carbon content is ferrite. The dark-etching constituent is pearlite which at higher powers has the appearance shown in Figs. 99 and 100.

Tensile Properties of the Steels illustrated.

Steels with less than 0·2 per cent. Manganese.	Yield Point, tons per sq. in.	Maximum Load, tons per sq. in.	Elongation per cent. on 2 ins.	Reduction of Area, per cent.
Normalised steels.				
Fig. 89. C. 0·15 per cent.	15	25	40	65
,, 90. ,, 0·3 ,,	16	28	35	60
,, 92. ,, 0·45 ,,	19	36	26	40
,, 93. ,, 0·6 ,,	20	43	20	20
,, 94. ,, 0·9 ,,	25	53	13	15
,, 95. ,, 1·20 ,,	36	62	8	8
,, 97. ,, 1·47 ,,	32	56	3	3
Annealed steels.				
Fig. 91. C. 0·3 per cent.	9	21	50	75
,, 99. ,, 0·89 ,,	17	37	4	4
,, 98. ,, 1·47 ,,	10	22	19	18
Normalised steel with 1·2 per cent. manganese.				
Fig. 100. C. 0·8 per cent.	40	68	15	15

Below this temperature the ferrite continues to be deposited in the magnetic condition.

On reaching 690° C. the remaining solid solution, represented by the point S, contains 0·9 per cent. of carbon. Here a considerable arrest (Ar_1) occurs in the rate of cooling while the solid solution breaks down into pearlite, the eutectoid mixture of α-iron (ferrite) and carbide of iron, Fe_3C (cementite).

Cooling of a 0·5 per cent. Carbon Steel.—The first arrest, Ar_3, now occurs at a lower temperature (750° C.), and the magnetic change point is coincident with it. The γ-iron solid solution deposits magnetic α-iron direct. Strictly speaking, therefore, there is no Ar_2 point, though this point is often regarded as merged into Ar_3, which is referred to as Ar_{23}. Further cooling, with deposition of ferrite from the solid solution, takes place until the remaining solution reaches the eutectoid composition, when Ar_1 occurs at about the same temperature as before (690° C.), but with a greater evolution of heat on account of the greater amount of carbon present.

Cooling of a 0·9 per cent. Carbon Steel.—In this steel no change occurs in constitution until Ar_1 is reached. The solid solution is exactly of eutectoid composition, and at Ar_1 (690° C.) it breaks down into pearlite with a still larger evolution of heat than occurs in the lower carbon steels.

Cooling of a 1·3 per cent. Carbon Steel.—On reaching a temperature of about 860° C., cementite or carbide of iron (Fe_3C) separates from the solid solution in a similar manner to the ferrite of a low-carbon steel. It forms a network enclosing grains of solid solution which on cooling become poorer in carbon and finally, on reaching Ar_1, attain the eutectoid composition and break down into pearlite.

Microstructure of Normalised or Annealed Steels.—By *normalising* is meant reheating a steel (however previously treated) to a temperature exceeding the upper limit of the critical range and allowing it to cool freely in air.

By *annealing* is meant reheating a steel for an appreciable time at a temperature exceeding the upper limit of the critical range, followed by slow cooling.*

The structure of normalised and of annealed steels consists of ferrite or cementite enclosing grains of pearlite. Figs. 88 to 97 show a series of normalised and of annealed steels of increasing carbon content.

The grain size of annealed steel is usually considerably larger than that of normalised steel. This is most frequently due to the higher maximum temperature employed in annealing, but even when the same maximum temperature is used the annealed steel will generally have a slightly larger grain size on account of the longer time it is maintained at that temperature. A more important difference between a steel in the normalised and in the annealed condition is to be found in the character and extent of the pearlite areas.

Pearlite was so called on account of the iridescent colours it shows and its resemblance to mother-of-pearl when viewed by oblique illumination. It consists of alternate lamellæ of ferrite and cementite (Fig. 99), and contains a little under 0·9 per cent. of carbon. Annealed steels containing less than 0·9 per cent. of carbon (hypo-eutectoid steels) consist of pearlite and ferrite; those with more than 0·9 per cent. carbon (hyper-eutectoid steels) contain pearlite and cementite. Since the whole of the carbon of a hypo-eutectoid steel (except less than 0·01 per cent., dissolved in the ferrite) is in the pearlite, the relative proportion of pearlite to ferrite in a pure carbon steel is as x is to $(0{\cdot}9 - x)$ where x is the percentage of carbon present. Thus, a 0·3 per cent. carbon steel should contain $\frac{1}{3}$ pearlite and $\frac{2}{3}$ ferrite; and a 0·45 per cent. carbon steel should contain $\frac{1}{2}$ pearlite and $\frac{1}{2}$ ferrite. These figures apply only to slowly cooled pure carbon steels. For a given carbon content the proportion of pearlite to ferrite is increased

* In general, *to anneal* means to soften or toughen by heating, but in the case of steel, *annealing* has the specialised meaning given above to distinguish it from *tempering* (p. 122). There are other specialised meanings indicated by the context, *e.g.* low-temperature annealing (pp. 118, 217).

by a more rapid rate of cooling, or by an increase in manganese (always present in commercial steels). Both of these impede the formation of lamellar pearlite, while manganese also has the effect of reducing the amount of carbon in the eutectoid.

Before making an estimate from the microstructure of the percentage of carbon present, the steel should be annealed (care being taken that no decarburisation occurs) and the probable effect of the manganese must be allowed for.

The difference in microscopical character of the pearlite of normalised and of annealed steels depends on the respective rates of cooling through the critical range. When the rate of cooling has been moderately rapid, complete lamination of the pearlite may not occur. An extremely fine and, at moderate magnification (*e.g.* 500), almost structureless pearlite is thus produced, which may be referred to as **sorbitic pearlite** (Figs. 26, 133, 134). When properly resolved under the microscope it bears little resemblance to sorbite, a constituent of hardened and tempered steels, which will be described later. This type of pearlite is induced by certain additions to the pure carbon steels, *e.g.* manganese. At low magnifications it has a brownish velvety appearance, and at very high magnifications is only partially resolved. Mechanically it is the strongest type of pearlite, and confers on a steel high elastic limit and considerable hardness.

The pearlite of normalised steel is finely lamellar (Fig. 101); that of annealed steel, cooled more slowly through the critical range, is more coarsely laminated (Fig. 99), but very coarse laminæ are structurally unstable and tend to ball up into coalesced particles of cementite in a groundmass of ferrite (Figs. 102 to 106). Increasing coarseness of the lamellar structure is accompanied by reduction in elastic limit, yield point and hardness.

By heating pearlite at temperatures just below Ac_1 (*e.g.* at 700° C.) for long times, or by employing a slow rate of cooling through the critical range, **granular pearlite** consisting of coalesced particles of carbide in a groundmass of ferrite, may

be produced (Figs. 102, 103). Prolonged treatment at 700° (especially in cold-worked steel) leads to the formation of **globular cementite,** in which the carbide has balled up completely into comparatively large masses (Fig. 104). In his condition the steel has the minimum hardness, and the lowest elastic limit and yield point possible for a given percentage of carbon. Hence this structure is frequently aimed at as a preliminary to severe cold-working of steel, *e.g.* spinning, cupping or the production of thin strip. The normal character of the pearlite can at any time be restored by heating the steel to a temperature well above the upper limit of the critical range and cooling in air (cf. Figs. 120, 121).

Cementite is a carbide of iron of the formula Fe_3C. It may occur in steel as free cementite (massive, network or globular) or as a constituent of the eutectoid, pearlite. Free cementite may occur in massive form in a low-carbon steel which has been cold-worked and subsequently annealed at about the temperature of Ac_1 (Fig. 148). It always exists in annealed steels with over 0·9 per cent. of carbon and occurs in the form of a continuous network in normalised steels with more than 1 per cent. of carbon (Fig. 95). Such a network of unyielding and brittle material has a detrimental influence on the strength and elongation of the steel. In very high carbon steels the network begins to form at a high temperature. If forging or rolling is continued to break up the network, and if the normalising temperature is insufficient to effect solution of the separated cementite, elongated or possibly rounded grains of cementite occur in the steel (Figs. 97, 110). In these forms, cementite, while retaining its hardening effect, has a less harmful effect on the elongation, and shows less tendency to embrittle the steel.

Prolonged heating of high-carbon steel at about 800° C. causes decomposition of cementite into graphite and ferrite (Fig. 98). The steel then gives a black fracture. Black tool-steel, heated to bright redness for a short time and quenched, is found to be fully hardened, showing that the

Normalised and annealed carbon steels.

FIG. 95.—Carbon 1·2 per cent., normalised; showing a white network of cementite, enclosing grains of pearlite.
Etched with 2 per cent. nitric acid in alcohol.
× 100.

FIG. 96.—The same steel etched with a boiling alkaline solution of sodium picrate. This reagent darkens the cementite, hence the reversal of etching effect. The darkened striæ in the lamellar pearlite are very fine and are not visible at this magnification. × 100.

FIG. 97.—Carbon 1·47 per cent. normalised, showing cementite (white network and needles) and pearlite.
Etched with 2 per cent. nitric acid in alcohol.
× 100.

FIG. 98.—The same steel after annealing for 72 hours at 800° C. The carbide has decomposed, giving nodules of graphite (black) embedded in ferrite grains, with some coarse pearlite remaining.
Etched with 5 per cent. nitric acid in alcohol.
× 100.

FIG. 99.—Eutectoid steel, containing 0·89 per cent. of carbon and very free from all impurities, annealed and slowly cooled, showing well-formed laminated pearlite.
Etched with 1 per cent. nitric acid in alcohol.
× 1000.

FIG. 100.—Steel containing 0·8 per cent. carbon and 1·2 per cent. manganese. Normalised, showing fine lamellar and sorbitic pearlite.
Etched with 1 per cent. nitric acid in alcohol.
× 1000.

PLATE XIX.

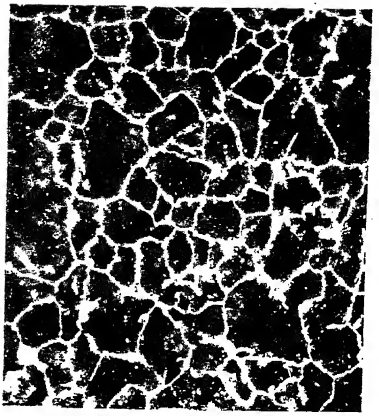


FIG. 95.

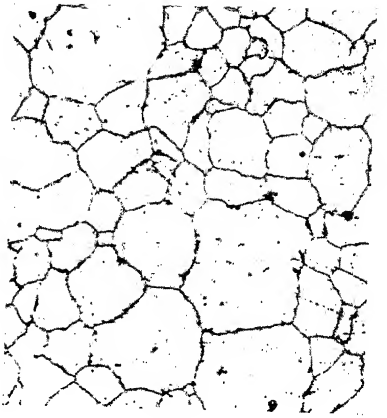


FIG. 96.

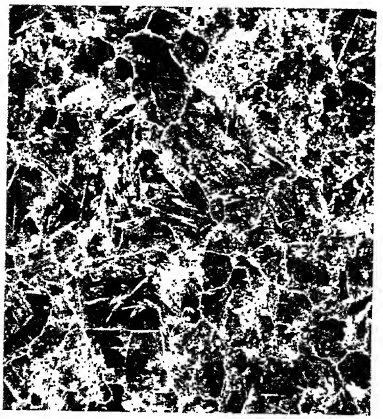


FIG. 97.

FIG. 98.

FIG. 99.

FIG. 100.

Fig. 101.

Fig. 102.

Fig. 103.

Fig. 104.

Fig. 105.

Fig. 106.

The structure of pearlite in carbon steels containing 0·45 per cent. carbon. Magnification, 1000 diameters.

FIG. 101.—Normalised. Ferrite and lamellar pearlite.

FIG. 102.—Cooled slowly through the critical range. Ferrite with lamellar and granular pearlite.

FIG. 103.—Cooled very slowly through the critical range. Ferrite and granular pearlite.

FIG. 104.—Cold-worked, reheated to Ac_1 for several hours and slowly cooled. Globular cementite in a groundmass of ferrite.

FIG. 105.—Ferrite and coarse lamellar pearlite, balling up into coalesced particles of cementite.

All the above were etched with 1 per cent. nitric acid in alcohol.

FIG. 106.—The same steel as in Fig. 105, etched with boiling alkaline solution of sodium picrate. The cementite is blackened.

The effect of the changes illustrated in Figs. 101 to 105 on the mechanical properties is to decrease the hardness, elastic limit, yield point, maximum load and ratio of yield point to maximum load. The elongation may be increased and the cold bend test remains satisfactory, but the impact figure is usually reduced.

carbon has re-dissolved, but the quality of the steel is permanently impaired.

On account of its great hardness, cementite frequently remains in relief in the polished section, and both "relief polishing" and "polish attack" may be used to display the microstructure of steels containing cementite. It is coloured brown or brownish black by etching with boiling sodium picrate solution, while ferrite remains unattacked (Figs. 96, 106).

Cementite may in certain circumstances closely resemble ferrite in appearance, but it may readily be distinguished from ferrite by:—

(1) Its appearance in relief. This may be detected under vertical illumination by difference in focus of the cementite particles and of the groundmass.

(2) The fact that strong etching with nitric acid stains ferrite, but leaves cementite quite bright.

(3) Its behaviour with the sodium picrate reagent.

(4) The fact that it rarely shows scratches. If a scratch is made on the specimen, it broadens in passing from pearlite to ferrite, but becomes narrow or disappears in passing across cementite.

Mechanical Properties.—With increase of pearlite (*i.e.* increase of carbon up to 0·9 per cent.) the hardness, tensile strength and elastic limit of steel increase, while elongation, reduction of area, and shock-resisting properties diminish. This change in properties is reflected in the uses to which untreated steels of various compositions are put:—

Carbon. Per cent.	Manganese. Per cent.	Approximate percentage of pearlite in the steel as used.	Uses.
0·10	0·3	10	Thin sheet, tinplate, etc.
0·15–0·20	0·5	20	Structural purposes, ship's plates.
0·20–0·25	0·5	25	Boiler plate.
0·30–0·35	0·7	40	Axles.
0·55–0·75	0·7	70–90	Tyres.
0·5	1·0	70	Rails.
0·6	1·0	80	Tramway rails.
0·65–0·75	0·8	90–100	High tensile wire.

Steels containing more than about 0·7 per cent. carbon are rarely used in the unhardened condition.

It is possible to form an approximate estimate from the microstructure of the strength of normalised or annealed carbon steels, based on the following figures (given by Arnold) for the properties of the constituents.

Micro-constituent.	Tensile strength. Tons per sq. in.	Elongation. Per cent. on 2 in.
Sorbitic pearlite . . .	70	10
Normal lamellar pearlite . .	55	15
Laminated pearlite . .	35	5
Ferrite	22	40

Thus for a steel consisting of p per cent. of normal lamellar pearlite, and f per cent. of ferrite,

$$\text{the approximate tensile strength} = \frac{1}{100}(22f + 55p) \text{ tons per sq. in.}$$

$$\text{and the approximate elongation} = \frac{1}{100}(40f + 15p) \text{ per cent. on 2 in.}$$

Such formulæ take no account of the influence of inclusions and are, of course, no guide to the properties of cold-worked material.

Austenitic Grain Size in Steel.—At temperatures above the upper limit of the critical range a steel exists as the γ-iron solid solution, consisting, as in the case of solid solutions stable at ordinary temperatures, of polyhedral grains. The passage from solid solution to ferrite and pearlite occurs on cooling without alteration of the grain size.

The ferrite is deposited in the grain boundaries of the solid solution, and if the cooling is sufficiently slow and the grain size is not too large a complete separation of ferrite in the form of a network occurs, enclosing grains which are entirely pearlitic.

If, however, the grains are very large, the rate of cooling may not be sufficiently slow to enable all the ferrite to diffuse to the grain boundaries. It then tends to separate within the grains, usually along the cleavage planes.

Such a structure was first observed in meteorites, and is known as the Widmanstätten structure. It is found in a

Carbon steel.

Etched with 2 per cent. nitric acid in alcohol. Magnification 100 diameters.

FIG. 107.—Steel billet, containing carbon 0·32 per cent., manganese 0·70 per cent., heated to the forging temperature and cooled, but not forged; showing Widmanstätten structure of ferrite (light) and pearlite (dark).

FIG. 108.—Steel containing carbon 0·4 per cent., manganese 0·75 per cent., overheated and slowly cooled, showing a coarse structure of ferrite and pearlite.

FIG. 109.—The same steel normalised and its grain size refined, showing a ferrite network enclosing grains of pearlite.

The effect on the properties is as follows :—

	As in Fig. 108.	*As in Fig.* 109.
Elastic limit, tons per sq. in.	14	20
Yield point, ,, ,,	19	23
Maximum load, ,, ,,	40	42
Elongation per cent. on 2 in.	24	29
Reduction of area per cent. .	41	49
Izod impact figure, ft.-lbs. .	6	18

FIG. 107.

FIG. 108.

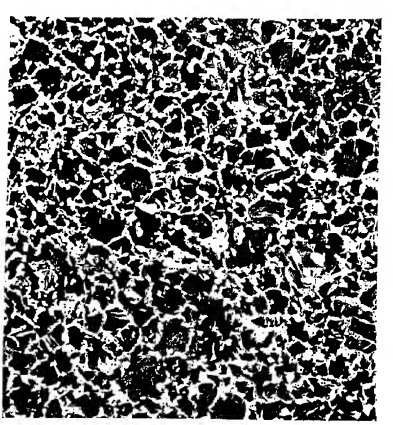


FIG. 109.

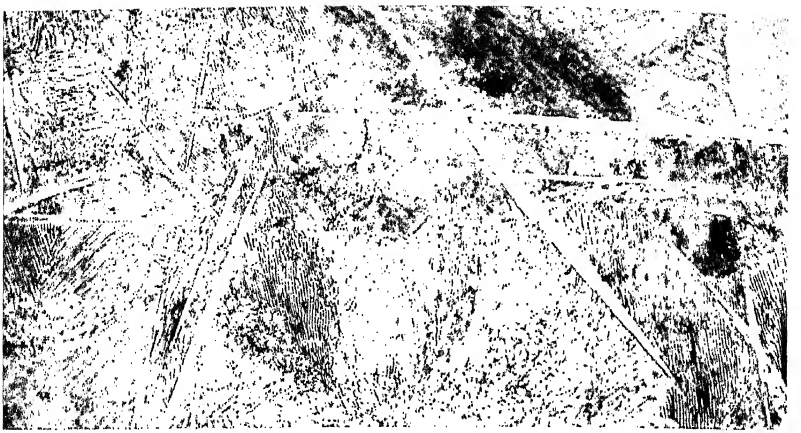


Fig. 110.

Fig. 111.

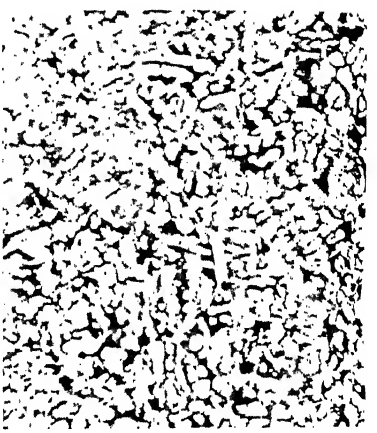
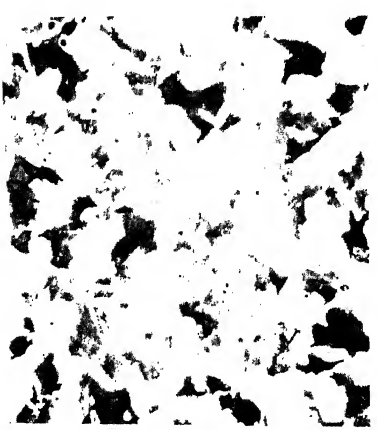


Fig. 112.



Carbon steels.

FIG. 110.—Carbon 1·2 per cent. As cast. Lamellar pearlite and needles of cementite which have separated on the cleavage planes of the original γ-iron solid solution. The same specimen at low magnification is shown in Fig. 40.

Etched with 2 per cent. nitric acid in alcohol. × 500.

Figs. 111 to 114 represent the structure of steel castings. Etched with 5 per cent. nitric acid in alcohol.

FIG. 111.—Cast steel (carbon 0·27 per cent., manganese 0·67 per cent.) showing acicular structure of ferrite as found in large castings. × 15.

FIG. 112.—Cast steel (carbon 0·24 per cent., manganese 1·08 per cent.) showing dendritic structure of ferrite frequently found in castings of small wall thickness. × 15.

FIG. 113.—Large casting (carbon 0·28 per cent., manganese 0·73 per cent.) originally acicular in structure, after being annealed at 950° C. and slowly cooled. × 100.

FIG. 114.—Small casting (carbon 0·36 per cent., manganese 1·16 per cent.) originally dendritic in structure, after being annealed at 900° C. and slowly cooled. The pearlite forms an incomplete network surrounding ferrite. × 100.

Mechanical Properties of the Steel Castings.

	Fig. 111.	Annd.*	Fig. 112.	Annd.*	Fig. 113.	Fig. 114.
Elastic limit, tons per sq. in.	8	14	10	21	15	19
Yield point, tons per sq. in.	14	18	17	23	17	23
Maximum load, tons per sq. in.	30·6	33·6	34·9	36·0	33·2	38·2
Elongation per cent. on 2 ins.	22	36	20	26	29	26
Reduction of area per cent.	24	54	27	36	34	35
Izod impact figure, ft.-lbs.	18	38	8	37	14	25
Brinell hardness number	142	152	160	165	143	161

* Tests made on small pieces cut from the castings and annealed at 875° C.

more or less pronounced state in steel castings and in steel which has been cooled from a very high temperature without being worked (Figs. 107, 108, 111).

On reheating a steel to a temperature immediately above Ac_3 recrystallisation with refinement of grain takes place (Fig. 58) as the solid solution is again formed, but as a rule the higher the temperature, above Ac_3, to which a steel has been heated the larger will be the grain size. The time for which the temperature is maintained has some effect, but the rate of growth after a short time becomes small compared with the influence of increasing temperature on the grain size. So much is this the case that it may be considered that for any steel there is at each temperature an approximately definite grain size, as indicated in the diagram (Fig. 115). A steel reheated to 1250° C. and cooled has a grain size represented by OL; one reheated only to 900° before cooling, by OK, etc. Hence normalising a coarse-grained steel refines the structure (Figs. 108, 109).

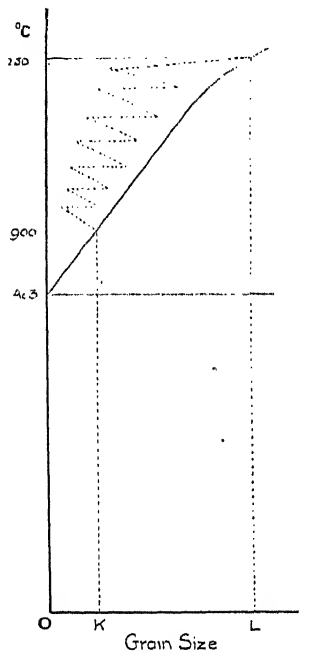


FIG. 115.—Diagram, for a Medium Carbon Steel, showing the Influence of Temperature on Grain Size and the Effect of Forging or Rolling (after *Howe*).

The grain size corresponding to a given temperature varies in different steels of apparently the same composition. Strong deoxidation with aluminium tends to raise the temperature at which rapid grain growth occurs, so that a given heat treatment results in a finer grain size. As the use of steel of controlled grain size facilitates uniform heat treatment and enables advantage to be taken, as may be desired, of the characteristics of fine-grain (enhanced toughness in the

notched-bar test, less tendency to warp or crack on quenching, less deterioration by strain-ageing) or of coarse-grain material (greater depths of hardening or of carburising, ease of machining), this property of aluminium has given rise to a method of control of inherent grain size, for the determination of which microscopical tests are required. The procedure for testing, standardised in America for many years, is described by Swinden and Bolsover * in a paper on "Controlled Grain Size," and a note on the principal test—the McQuaid–Ehn test—is appended to this Chapter.

Hot- and Cold-working of Steel.—Steel possesses a large grain size at the temperature to which it is heated for such operations as forging, rolling or similar work. As work is done on the steels, the grains are deformed and broken up, but rearrangement of the crystal structure proceeds simultaneously. The temperature, however, is meanwhile falling, and the re-formed grains tend to grow to the normal size corresponding to that temperature. In the course of this growth they are again broken up by rolling or forging, as shown by the dotted line in the diagram (Fig. 115), and the ultimate grain size is dependent on the temperature from which the steel cools after forging or rolling. Thus, normalising may be dispensed with if rolling is finished at the normalising temperature.

If the finishing temperature is below Ar_3 some separation of ferrite from the solid solution will have occurred and subsequent deformation will have the effect of elongating the ferrite and pearlite grains (Figs. 116, 117). The temperature may still be such that readjustment to equi-axial grains occurs in the banded structure of the ferrite and pearlite, and the hardening effect of cold-work may not be apparent. While the occurrence of a structure which is uniform in three directions at right angles to one another is evidence of a finishing temperature above Ar_3, a pronounced banded structure is not necessarily an indication of a finishing temperature

* *Journal of the Iron and Steel Institute*, 1936, (2), vol. cxxxiv, p. 457.

Carbon steels.

All etched with 1 per cent. nitric acid in alcohol.

FIG. 116.—Mild steel plate, carbon 0·2 per cent., longitudinal section showing effect of rolling. × 100.

FIG. 117.—Medium carbon steel rod, carbon 0·5 per cent., manganese 1·0 per cent., longitudinal section showing effect of rolling. × 100.

FIG. 118.—Cold-drawn carbon steel wire, carbon 0·75 per cent., manganese 0·75 per cent., longitudinal section, showing great deformation of the original structure of sorbitic and fine lamellar pearlite. × 1000.

There is no change in the appearance of the microstructure on annealing at temperatures of 200° to 300° C., a treatment which improves the elastic properties without reducing the tensile strength below 100 tons per sq. in.

FIG. 119.—The same wire reheated to 500° for ½ hour and cooled in air. The carbide has begun to coalesce, and the ferrite to recrystallise, giving a structure of fine particles of carbide in a groundmass of ferrite with a tensile strength of 78 tons per sq. in. × 1000.

FIG. 120.—The same wire reheated to 650° C. for ½ hour, and cooled in air. Further coalescence of the carbide and complete recrystallisation of the ferrite have occurred with a fall of tensile strength to 53 tons per sq. in. × 1000.

FIG. 121.—The same wire annealed, showing fine lamellar pearlite and some ferrite. Tensile strength, 49 tons per sq. in. × 1000.

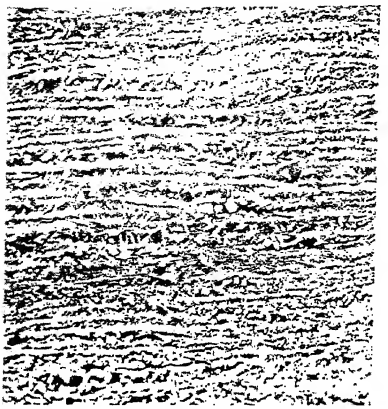


FIG. 116.

FIG. 117.

FIG. 118.

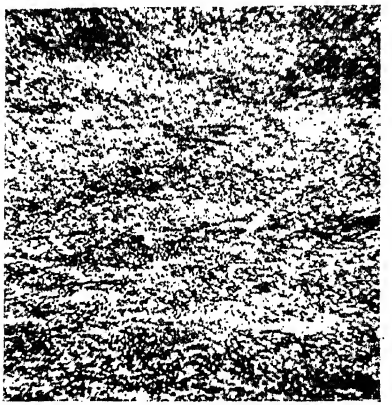


FIG. 119.

FIG. 120.

FIG. 121.

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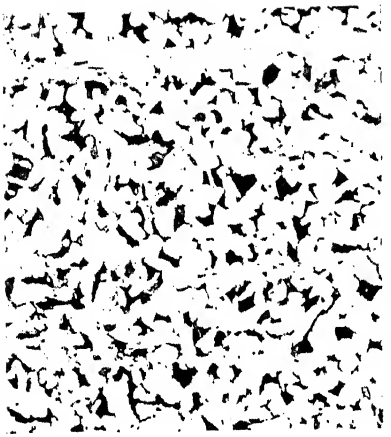


Fig. 122.

Fig. 123.

Fig. 124.

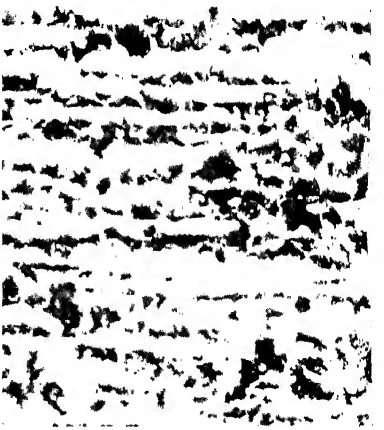
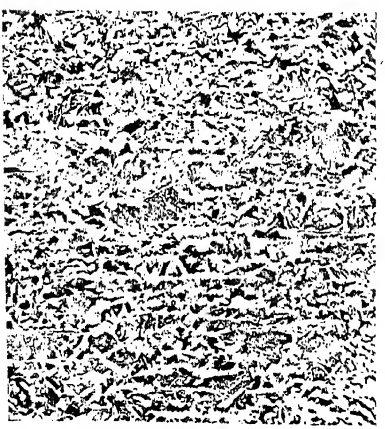


Fig. 125.



Effect of manganese on the properties of steel.
Longitudinal sections.
Etched with 2 per cent. nitric acid in alcohol.

The steels represented in Figs. 122 to 124 contain 0·23 per cent of carbon, and have been normalised from 890° C. in the form of $\frac{3}{4} \times 1\frac{1}{2}$ inch bar.

FIG. 122.—Manganese 0·37 per cent. The usual ferrite and pearlite structure. × 100.

FIG. 123.—Manganese 1·42 per cent. The amount of pearlite is considerably greater, and the separation of ferrite, forming a fragmentary network, has been less complete. × 100.

FIG. 124.—Manganese 2·10 per cent. The grain size is much finer and the separation of ferrite less complete. The ferrite shows a tendency to acicular structure, having separated on the cleavage planes of the original austenite grains. The air-hardening tendency is shown by the marked fall in elastic limit and in impact figure which accompanies the increase in hardness. × 100.

FIG. 125.—The same steel as shown in Fig. 123 cooled from 890° C. at a rate (at 700° C.) of 14° per minute. Much more complete separation of ferrite has occurred, and the pearlite occupies little more area than in Fig. 122. × 100.

FIG. 126.—Commercial high tensile steel plate ($\frac{3}{4}$ inch thick), containing 0·29 per cent. carbon, and 1·60 per cent. manganese, hot rolled and cooled in air from the finishing temperature (above Ar_3). × 100.

FIG. 127.—The same steel as in Fig. 126 showing the finely lamellar structure of the pearlite. × 1000.

Mechanical properties associated with the structures illustrated.
Longitudinal tests.

	Fig. 122.	Fig. 123.	Fig. 124.	Fig. 125.	Fig. 126.
Carbon, per cent.	0·22	0·23	0·23	As Fig. 123 slowly cooled.	0·29
Manganese, per cent.	0·37	1·42	2·10		1·60
End of Ac_3	855° C.	820° C.	810° C.		—
Elastic limit, tons per sq. in.	11	16	11	14	17
Yield point, tons per sq. in.	16·8	22·8	26·6	21·0	23·9
Maximum load, tons per sq. in.	28·1	37·3	45·9	36·0	41·7
Ratio of yield point to max. load	0·60	0·61	0·58	0·58	0·57
Elongation per cent. on 2 ins.	39	35	23	32	31
Reduction of area, per cent.	66	69	43	62	68
Izod impact figure, ft.-lbs.	79	66	16	57	40
Brinell hardness number	126	167	210	159	183

below Ar_3, since segregation (especially of phosphorus) gives rise to a similar effect in rolled steel. By slowly cooling from above Ar_3, and so allowing time for diffusion of carbon out of the regions of high phosphorus content, a banded structure can often be produced in a steel which apparently shows equi-axial crystals after air-cooling from the same temperature (Fig. 125).

If the process of working is continued below a visible red-heat, strain-hardening is produced. The object of cold-working at ordinary temperatures is to obtain and utilise the properties of steel in a condition of very severe strain-hardening. To carry out this process efficiently on medium-carbon steels it is advisable to secure a uniform structure of fine sorbitic pearlite by heating to 950° to 1000° C. and cooling fairly rapidly (" patenting ").

The severely cold-worked condition (Fig. 118) is characterised by a high yield point and great hardness, but the elastic limit is usually low. Cold-drawn material which is required to maintain a constant stress (*e.g.* piano wire, stays, and struts) should never be put to work in this over-strained condition, but should be subjected to a low-temperature heat treatment which raises the elastic limit and restores the elastic properties, at the same time increasing the yield point and hardness slightly. The microscope fails to distinguish between overstrained steel and the same steel aged or restored by low-temperature annealing, but momentary heating to 500° or prolonged annealing at temperatures above 350° causes softening, and has a marked effect on the structure (Figs. 119 to 121).

High Tensile Structural Steels.—It is desirable to employ the term *structural steels* to mean steels used in the untreated condition for bridges, girders, ship plates, etc., and to retain the term *constructional steels* for those used most frequently in the heat-treated condition in automobile and aeroplane construction and for general engineering purposes.

With the increasing demand for higher tensile properties in steels for modern structures, considerable development has

occurred in structural steels and sections for which mild steel was at once time exclusively employed.

Greater ductility with little or no change in tensile strength is achieved by the addition to very mild steel of an element the main function of which is to form a solid solution in the ferrite, as, for example, by the addition of silicon in the high silicon mild steels developed in Germany.

The alternative, more commonly favoured, is to increase the tensile strength, and in particular the elastic limit, while retaining an equal or but slightly reduced elongation. To do this the mere strengthening of the ferrite is not sufficient; it is necessary to add an element which will increase the ratio of pearlite to ferrite in the air-cooled steel. If this is done by increasing the carbon content above 0·3 per cent., the ferrite, though reduced in amount, is unaffected in character and the increased strength is accompanied by a considerable reduction in ductility.

The composition regarded with most favour is one containing 1·2 to 1·6 per cent. of manganese with 0·25 to 0·30 per cent. of carbon (Fig. 126). In addition to modifying the properties of the ferrite, manganese increases the ratio of pearlite to ferrite in the air-cooled steel (Figs. 122 to 125) and produces a more finely lamellar pearlite (Fig. 127). With 0·3 per cent. of carbon, a manganese content higher than 1·6 per cent. gives rise to air-hardening properties which prevent the steel being used in the "as rolled" condition.

Other steels have been employed or suggested, *e.g.* 3 per cent. nickel steel (used on a large scale), silico-manganese steels, 0·5 per cent. chromium steel, chromium–copper steels, etc., but in all cases their structure must consist of ferrite and pearlite (finely lamellar or sorbitic). Absence of ferrite, or any indication that a martensitic constituent is replacing pearlite in the rolled or normalised material, means that, though the properties may be excellent in the heat-treated condition, the steel is unsuitable for use as an untreated or normalised structural steel.

Practical Notes

Polishing.—The usual method, finishing off with diamantine, wet.

Etching.—A 2 per cent. solution of nitric acid in alcohol or a 5 per cent. solution of picric acid in alcohol.

Time of etching for ordinary examination, about 30 seconds. For examination of pearlite at high magnifications, about 10 seconds (or preferably a 1 per cent. solution of nitric acid in alcohol for 30 seconds). To show ferrite grains in low-carbon steel, 1 or 2 minutes or stronger solutions may be used (*cf.* wrought iron).

To reveal cementite in steels containing free cementite, sodium picrate etching is most useful, but polish attack and polishing in relief (p. 18) may be used in certain cases.

Alkaline solution of sodium picrate (Kourbatoff).—Two grams of picric acid are digested for ½ hour with 100 c.c. of water in which 25 grams of caustic soda are dissolved, and the supernatant liquid is poured off.

The polished specimen is placed in a porcelain dish and covered with the solution, which is heated to boiling for 5 to 10 minutes. The section is washed with water and examined. The attack may be repeated if necessary. Staining, if encountered, may be prevented by avoiding exposure of the etched surface to air while hot, *i.e.* by directing a stream of water into the dish containing the specimen immersed in the etching reagent.

The McQuaid–Ehn Test for austenitic grain size (American Society for Testing Materials Standard E 19–33) is carried out as follows :—*

A specimen is selected of a suitable size to obtain a convenient microsection when parted into two. All scale is removed from the specimen either by filing or grinding. The sample is packed in a box containing good carburising compound (" Hardenite " is recommended). It is important that

* As described by Swinden and Bolsover, *loc. cit.*

the box should be adequately sealed, as otherwise carburising gases will escape and prevent the formation of a hypereutectoid zone. The box and contents are heated in 2 hours to, and soaked for 6 hours at, 927° C. (1700° F.), and then allowed to cool slowly down to 400° C. or less before emptying. The temperature should be regular within ± 5° C. A section is cut from the sample, polished on the cut face and etched with boiling alkaline sodium picrate solution. The carburised case has then a clearly defined grain size, which is examined on a projection microscope at a magnification of 100 diameters. Comparison of the projected field with those given on a standard chart which shows typical fields for each grain size, enables the inherent grain size to be assessed. There is considerable latitude as regards time at carburising temperature, temperature to which the specimens are cooled before withdrawal from the furnace and carburising temperature, within which there is no significant difference in the resulting grain-size value. It is, however, desirable to maintain standard conditions as far as possible.

If n = number of grains per sq. in. at a magnification of 100, and N = grain-size index: then $n = 2^{N-1}$.

Thus, for—

grain-size 2, $n = 2^1 = 2$; limits, 1·5 to 3 grains per sq. in.
„ 7, $n = 2^6 = 64$; „ 48 to 96 grains per sq. in.

CHAPTER VIII

THE STRUCTURE AND PROPERTIES OF HARDENED AND TEMPERED CARBON STEELS

When steel is heated to a temperature above the upper limit of its critical range, and is then rapidly cooled in a suitable medium such as water or oil, it is *hardened*. An increase in hardness is observable even when the carbon percentage is low, and this increase is greater the more rapid the cooling. The yield point and toughness of mild steel containing about 0·10 to 0·15 per cent. of carbon are greatly improved by water quenching from the normalising temperature instead of cooling in air. If the carbon is more than 0·3 per cent., the increase in hardness is very appreciable, and with identical rates of cooling the hardness increases with increase of carbon, at any rate up to 1 per cent., but it is accompanied by increasing brittleness.

The hardened article is usually too brittle for use, and is therefore tempered in order to reduce its hardness and increase its toughness.

By *tempering* is meant reheating a steel (however previously treated) to a temperature not exceeding the lower limit of its critical range, followed by either rapid or slow cooling.

The higher the temperature of tempering, the more does the treated steel approach its condition of minimum hardness, but after identical hardening and tempering treatment, the higher the carbon content the greater is the final degree of hardness of the steel.

With the aid of the constitutional diagram of the iron-carbon alloys (Fig. 82) it is possible to trace and interpret the changes which occur in the microstructure of the steel during the treatment outlined above.

Uniform Slow Heating to a High Temperature.—Annealed steels, consisting of grains of pearlite enclosed in a ferrite or cementite network, do not change in constitution until a temperature is reached at which the constituents of the pearlite mutually dissolve to form a solid solution containing 0·9 per cent. of carbon, leaving the free ferrite or cementite intact. This change occurs with an absorption of heat, which is greater the higher the carbon content, causing an arrest Ac_1 in the heating curve, which takes place at approximately the same temperature for all pure carbon steels. As the temperature is raised the free ferrite or cementite is progressively absorbed into solid solution. Solution of the ferrite network in hypo-eutectoid steels cannot be complete until Ac_3, the upper limit of the critical range, is reached. The temperature required will therefore be higher for the 0·3 than for the 0·5 per cent. carbon steel, and in the former case the ferrite undissolved at the temperature Ac_2 will change to the non-magnetic condition before completely passing into solution. Above Ac_3 (provided equilibrium has been attained) the steel consists entirely of solid solution of carbon in γ-iron and is in a condition suitable for hardening, but an appreciable time must be allowed to effect complete solution of the ferrite network or to obtain equilibrium conditions in large masses. Similarly a steel of higher carbon content is in a condition suitable for hardening as soon as complete mutual solution of ferrite and carbide has been attained.

Rapid Cooling from a High Temperature.—Very rapid cooling by quenching from any given temperature tends to retain the steel in the structural condition in which it existed at that temperature. The less drastic the quenching and consequently the slower the rate of cooling the greater is the possibility of change. In carbon steels, the γ to α change always occurs, however drastic the quenching, and the microscopical constituents observed in the quenched steels are more or less advanced decomposition products of the original solid solution.

Austenite (Fig. 128).—Study of various alloy steels leads to the conclusion that the micrographical structure corresponding to the solid solution which exists at high temperatures is that known as austenite, a structure which cannot be retained by even the most rapid quenching of carbon steels. When obtained in a homogeneous form in alloy steels it consists of polyhedral grains frequently showing twinning. It has never been obtained in a pure carbon steel. The presence of about 1·5 per cent. of manganese together with high carbon renders it possible to obtain a mixture of austenite and martensite by very rapid cooling.

The generally recognised stages of decomposition of austenite are given in the following table.

STAGES OF DECOMPOSITION OF THE γ-IRON–CARBON SOLID SOLUTION.

AUSTENITE *

On tempering at progressively higher temperatures below the critical range, yields	On cooling at progressively slower rates through the critical range is replaced by †
MARTENSITE	MARTENSITE
TROOSTITE	TROOSTITE
SORBITE (minutely granular)	SORBITIC PEARLITE (minutely lamellar)
FINE COALESCED CARBIDE in a groundmass of FERRITE	LAMELLAR PEARLITE
COARSE COALESCED CARBIDE in a groundmass of FERRITE	GRANULAR PEARLITE

* The pure γ-iron–carbon solid solution has never been obtained at atmospheric temperatures.

† Together with a progressively more complete separation of free ferrite or free cementite according as the carbon is less or more than the eutectoid composition.

The Products of Quenching

Martensite (Figs. 129 to 132, 139, 143, 156) is the most important constituent of hardened (untempered) steel. In steel of any given composition it is the hardest of the possible constituents obtained by heat treatment. In its formation the allotropic change γ- to α-iron has been completed, but the

carbon (or carbide) remains in almost as highly dispersed a condition as in the solid solution, austenite. A characteristic feature of the structure is that it may be resolved under high powers into intersecting systems of straight parallel lines, marking the cleavage or gliding planes of the original solid solution.

Troostite is a structureless black-etching constituent. The carbide, though still irresolvable, is less highly dispersed than in martensite. Troostite is produced when the rate of cooling is less rapid than that required to produce martensite. Steel quenched from Ac_1, while the change is in progress, consists of troostite, either alone or with ferrite or cementite according to composition (Figs. 136 to 138). When quenching from a higher temperature has been sufficiently rapid to obtain martensite, ferrite or carbide still tend (if the carbon content is far removed from that of the eutectoid) to segregate into regions which appear as troostite. A ring of troostite may surround any small particles of ferrite or carbide which have separated under such conditions or have remained undissolved at the hardening temperature. Troostite may occur as very fine needles outlining the structure of martensite (troosto-martensite, Figs. 130, 153), or in larger masses in the martensite (Figs. 131, 138), or as an incipient grain boundary (Fig. 143). With less severe quenching, a structure intermediate between troostite and sorbitic pearlite is formed (Fig. 132). This, when resolved, frequently shows a nodular formation of very fine lamellæ of ferrite and cementite radiating from a nucleus.

Sorbitic Pearlite.—(Figs. 133, 134). If the rate of cooling is still slower (as, for example, that of large masses in oil, or of smaller specimens in hot water, or in an air blast) opportunity is afforded for the separation of more ferrite or cementite from the solid solution, though the final separation of the eutectoid, pearlite, is partially suppressed. The lamellar pearlite formed on slow cooling is replaced by grains of sorbitic pearlite. In a hypo-eutectoid steel, owing

Austenite, martensite, troostite and sorbitic pearlite.
All etched with 1 per cent. nitric acid in alcohol.

FIG. 128.—Austenite, showing twinning, in a steel containing carbon 0·5 per cent., nickel 24·4 per cent. × 100.

FIG. 129.—Austenite grains, showing an internal structure of martensite in a tungsten steel containing carbon 1·2 per cent., tungsten 3·0 per cent., heated to 1200° C., slowly cooled to 750° C. and then air-cooled. × 500.

FIG. 130.—Troosto-martensite (martensite with needles of troostite) in a 0·6 per cent. carbon steel quenched in water from 800° C. × 1000.

FIG. 131.—Martensite and troostite in a rapidly cooled steel containing carbon 0·73 per cent., manganese 1·70 per cent. × 1000.

FIG. 132.—Martensite and troostite in steel containing carbon 0·40 per cent., manganese 0·42 per cent., quenched in oil. × 1000.

FIG. 133.—Sorbitic pearlite in a 0·9 per cent. carbon steel quenched from 760° C. in warm water. × 1000.

FIG. 128.

FIG. 129.

FIG. 130.

FIG. 131.

FIG. 132.

FIG. 133.

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FIG. 134.

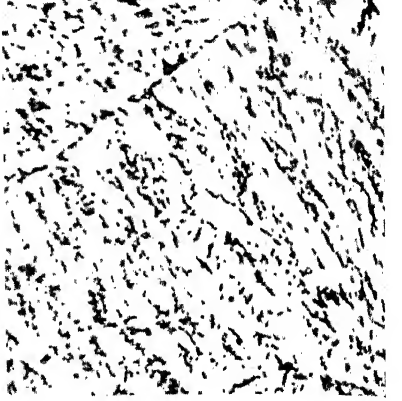


FIG. 135.

FIG. 136.

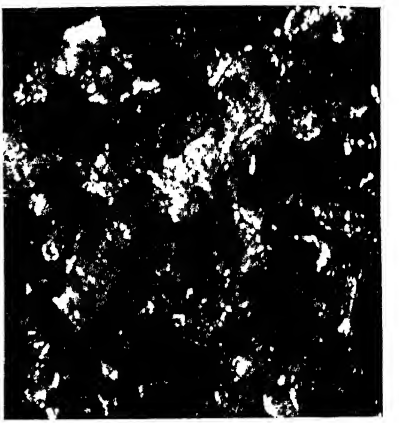


FIG. 137.

FIG. 138.

Distinction between sorbitic pearlite and sorbite.
All etched with 1 per cent. nitric acid in alcohol.

FIG. 134.—Sorbitic pearlite, when resolvable, is finely lamellar. This structure is formed at Ar_1 and can only be produced if the rate of cooling through the critical range is insufficiently great to depress the temperature of the Ar_1 change. × 4000.

FIG. 135.—Sorbite is granular. It is formed from martensite or troostite at a temperature below Ac_1, and its presence indicates that when the steel was last cooled through the critical range, the rate of cooling was sufficiently great to depress the temperature of the Ar_1 change and so prevent the formation of pearlite. × 3000.

Transition from pearlite to martensite.

Figs. 136 to 139 represent changes in structure produced in a short interval along the length of a bar of carbon steel, quenched in water when one end was above and the other end below the temperature of the critical range. Starting from the end which was colder, we have—

FIG. 136.—Lamellar pearlite (the original structure) and troostite.

FIG. 137.—Troostite.

FIG. 138.—Troostite and martensite.

FIG. 139.—Martensite. × 2000.

to the partial suppression of the separation of ferrite on cooling, these grains occupy a far larger area than the pearlite grains in the slowly cooled steel. Sorbitic pearlite, if resolvable, has an exceedingly fine lamellar structure, but it is often irresolvable under the microscope and frequently etches dark very rapidly, in which case it is known as troosto-sorbite. It is possible for lamellar and sorbitic pearlite and troosto-sorbite to occur together in the same steel cooled at a rate not sufficiently slow to give lamellar pearlite only.

The Products of Tempering

Martensite.—A mild tempering of some alloy steels obtained in the austenitic condition by quenching gives martensite, structurally similar to that produced by quenching. The change is accompanied by an increase in hardness.

Troostite.—A mild tempering of quenched martensitic carbon or alloy steels gives rise to troostite structurally similar to that obtained by rapid quenching, but the nodular (radially laminated) form of troostite cannot be formed by tempering. The change from martensite to troostite is accompanied by a slight fall of hardness and an increase in toughness. Troostite is found in properly hardened and tempered cutting tools, chisels, knives, etc.

Sorbite is the essential constituent of hardened and tempered steels intended for constructional purposes. The sorbite in this case is not sorbitic pearlite: its structure when resolvable is minutely granular, and not lamellar. It is formed by the gradual breakdown of martensite resulting in a uniform distribution of minute particles of carbide in a groundmass of ferrite (Figs. 135, 144, 157, 162). If tempering is carried on at a temperature too near to the critical point, or if the steel is soaked for too long a time, coalescence of the carbide continues until relatively large particles are formed (Fig. 147). Free ferrite or carbide in the form of a network can never be formed on tempering. If found in

hardened and tempered steel it must have survived through, or been formed during, the hardening operation.

Heat-treated Medium-Carbon Steels (0·3 to 0·75 per cent. carbon).—The uses to which these steels are put include :—

Carbon per cent.	Uses.
0·3–0·4	Propeller shafts, axles, crankshafts.
0·5–0·7	Springs.
0·7–0·75	Dies.

The practical limits of temperature of heat treatment are fixed by two points on the heating curve of the steel, the beginning of Ac_1 and the end of Ac_3. In heating for hardening, Ac_3 must be exceeded by a reasonable margin; in heating for tempering, Ac_1 must not be too closely approached. Treatment at any temperature between these limits is detrimental to the mechanical properties and must be avoided.

Steel is not in a condition suitable for hardening until complete solution of the ferrite and carbide has been attained. In some cases of large forgings of medium-carbon steel, a preliminary normalising or annealing is necessary to refine the coarse forging structure, and bring the ferrite into a condition in which it will more readily pass into solution. The temperature of hardening should be well above the critical range, to ensure that no part of the article is below Ac_3, otherwise the ferrite will not be wholly dissolved (Fig. 142). On the other hand, hardening from a very high temperature induces a coarse structure and associated brittleness, and may also reduce the rate of cooling through the critical range.

For successful hardening, the rate of cooling through the critical range should be sufficiently rapid to lower Ar_1 and prevent the formation of pearlite. Heat is only abstracted by the quenching medium from the surface of the steel. The rate of cooling of the interior is dependent on the rate of diffusion of heat to the surface. Hence large forgings are, whenever possible, bored before treatment to reduce the

can be obtained. A coarse grain size indicates that the preliminary annealing has been omitted or that overheating has occurred on hardening. Such a structure renders the steel very liable to crack on quenching.

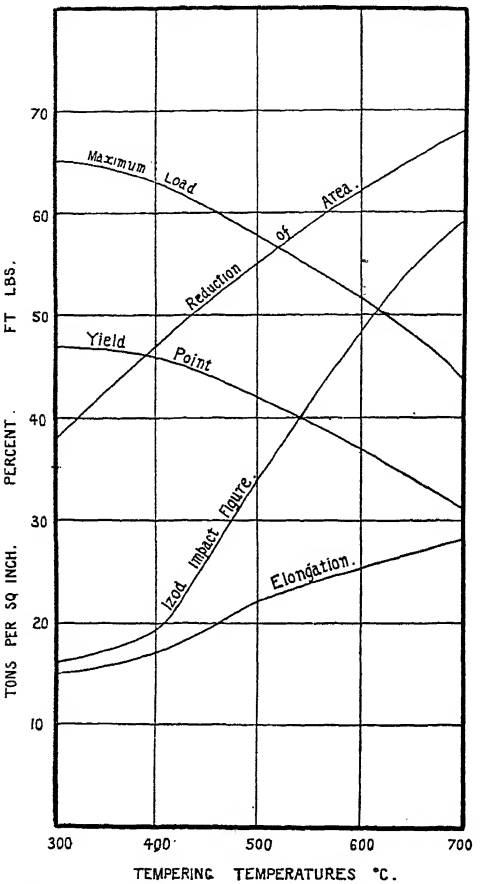


FIG. 140.—Mechanical Properties of a 0·45 per cent. Carbon Steel, Water-hardened from 870° C. in the form of $1\frac{1}{8}$ in. Diameter Bars, and Tempered for $\frac{1}{2}$ hr. at Various Temperatures. (*Institution of Automobile Engineers, Steel Research Committee.*)

To reduce brittleness the steels are tempered, usually at comparatively low temperatures. A possible source of brittleness (which cannot be removed by tempering) is the presence of an excess of massive cementite, due to an insufficient refining or hardening temperature, or possibly to the use of

steel with too high a carbon content. Free cementite in masses of considerable size should not occur in cutting tools which have to withstand any degree of rough usage. The essential micro-constituents of such steels are martensite, troosto-martensite, and troostite, increasing in proportion in the order given as the amount of rough usage to be endured increases.

Local Hardening.—Machine parts which have to withstand wear are sometimes made of medium-carbon steel locally hardened or surface-hardened by means of the oxy-acetylene flame.

Except in the case of perfectly smooth surfaces, spot-hardened, the article is usually tempered to a straw colour to avoid excessive brittleness of the hardened portion. Microscopical examination of the border-line between the hardened and unhardened regions generally yields interesting results. The ferrite network present in the unhardened region persists in a fragmentary form for some distance into the hardened steel, although the enclosed grains of pearlite have been transformed into solid solution (Figs. 149, 150). Regions which have attained a temperature above Ac_1 and below Ac_3 still contain ferrite. The effect is more pronounced in lower carbon steels, since the thicker ferrite network requires a longer time above Ac_3 to pass completely into solution.

Case Hardening has for its object the production of a hard skin on a tough mild steel core. It is an adaptation of the old cementation method of steel making in which carburisation of iron was effected by prolonged heating in contact with carbonaceous material. Diffusion of carbide occurs on heating under these conditions at temperatures above 900° C., and the resulting material may show a gradation of carbon content from, say, 1 per cent. at the skin to the original figure of 0·1 or 0·2 per cent. at the core, revealed in the microstructure of the untreated material as :—

A decreasing amount of cementite, with pearlite	Pearlite	Pearlite with an increasing amount of ferrite.

Heat treatment of a carbon steel containing carbon 0·33 per cent., manganese 0·54 per cent.

Critical points on heating $\begin{cases} Ac_1 \text{ max. } 732^\circ \text{ C.} \\ Ac_3 \text{ ends } 814^\circ \text{ C.} \end{cases}$

All etched with 2 per cent. nitric acid in alcohol. Magnification 250 diameters.

FIG. 141.—Slowly cooled from 900° C. Ferrite, and fine lamellar pearlite. Brinell hardness 136.

FIG. 142.—The steel of Fig. 141 heated to 775° C. and quenched in oil. At Ac_1 the ferrite and carbide of the pearlite pass into solid solution which subsequently absorbs some of the ferrite, but however long the steel is held at 775° C. (below Ac_3) some ferrite must remain unabsorbed. After cooling in oil the structure consists of ferrite and sorbitic pearlite. Brinell hardness 210.

FIG. 143.—The steel of Fig. 141 heated to 900° C. and quenched in water. At this temperature (above Ac_3) solution of ferrite is complete, and the structure of the small quenched specimen shows martensite and troostite. Brinell hardness 390.

FIG. 144.—The steel of Fig. 143 heated to 730° C. and slowly cooled. Heating to this temperature (immediately below Ac_1) results in a coarse sorbitic structure consisting of particles of carbide in a groundmass of ferrite. Brinell hardness 170.

FIG. 145.—The steel of Fig. 144 heated to 745° C. and slowly cooled. Above Ac_1 solid solution is again formed round the coalesced carbide particles, and some pearlite is formed from this on cooling, but the separation of pearlite into compact areas is not complete. Brinell hardness 142.

FIG. 146.—The steel of Fig. 145 heated to 830° C. and slowly cooled. The uniform solid solution formed above Ac_3, on cooling deposits ferrite between Ar_3 and Ar_1, and finally passes into lamellar pearlite at Ar_1, giving a structure of ferrite and pearlite of smaller grain size than that of the original specimen (Fig. 141) cooled from 900° C. Brinell hardness 136.

FIG. 141.

FIG. 142.

FIG. 143.

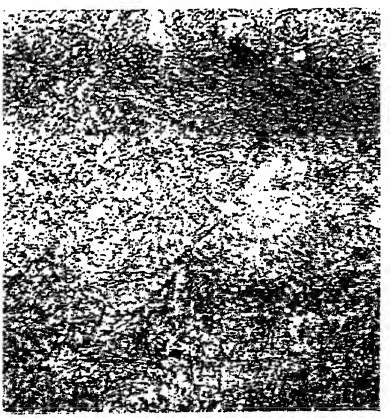


FIG. 144.

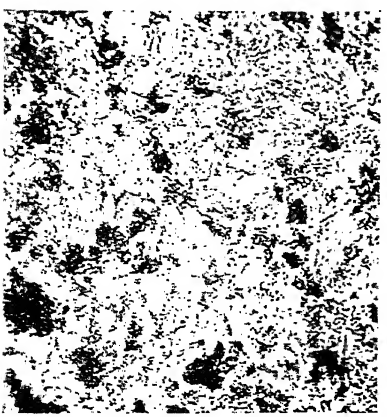


FIG. 145.

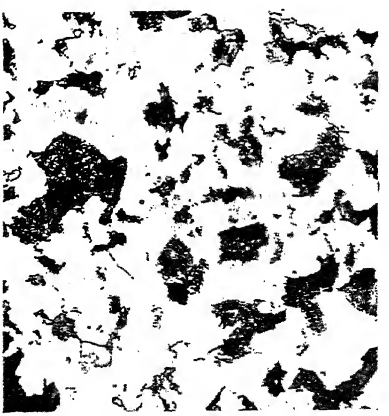


FIG. 146.

PLATE XXVIII.

FIG. 147.

FIG. 148.

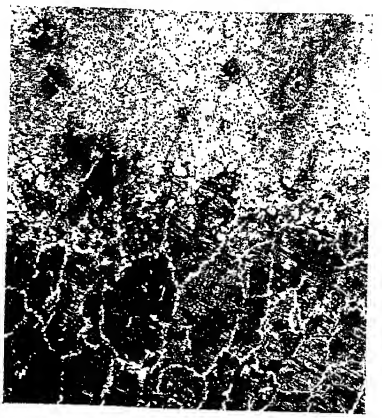
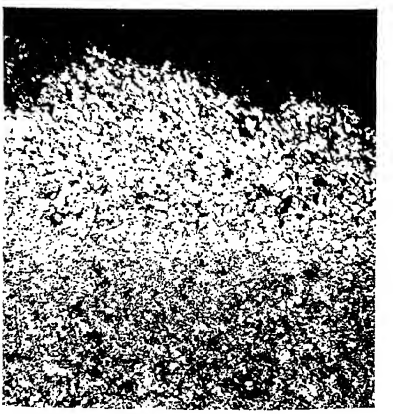


FIG. 149.

FIG. 150.

FIG. 151.



All etched with nitric acid in alcohol.

FIG. 147.—Steel containing 0·4 per cent. of carbon, oil-hardened, reheated to Ac_1 and slowly cooled, showing coarse coalesced carbide in a groundmass of ferrite. × 1000.

FIG. 148.—Massive cementite in a 0·1 per cent. carbon steel which has been cold-worked, then heated just above Ac_1 and cooled very slowly through Ar_1. The steel is mainly pure ferrite, with some scattered regions (such as that shown) into which the carbide has coalesced. × 1000.

FIG. 149.—Steel containing 0·6 per cent. of carbon locally hardened by a blowpipe flame, showing the junction between the hardened and unhardened region. Ferrite network enclosing grains of pearlite below: fine martensite with some undissolved ferrite above. × 100.

FIG. 150.—Steel containing 0·4 per cent. of carbon, locally hardened. Undissolved ferrite remaining in the hardened region, which consists of slowly etching martensite above: ferrite and granular pearlite below. × 250.

FIG. 151.—Case-hardened mild steel, heat-treated, showing an outer skin of slowly etching martensite, succeeded by a band of troostite, with a central core showing a sorbitic structure. × 50.

FIG. 152.—Mild steel, case-hardened and heat-treated, but decarburised during the treatment. The outer skin now consists of ferrite, with a few troostitic regions, and is softer than the sorbitic steel below. × 50.

To obtain the best properties the steel is then hardened. A temperature of less than 800° C. must be used to harden the high-carbon steel case, or its grain size will be too coarse; but this is below that needed to refine the structure of the mild steel core. A double treatment is therefore necessary: heating to 900° or 950° C. and air-cooling or quenching to refine and toughen the core, followed by heating to 750° or 800° C. and quenching to harden the case. This treatment results in the following structure (Fig. 151):—

Core :—Fine-grain ferrite, and troostite.
An intermediate layer of troostite.
Case :—Martensite, and possibly cementite.

Free cementite in large amounts or in a continuous network is a source of weakness giving rise to surface cracks, flaking, etc.

Practical Notes

Polishing.—The usual method finishing with diamantine, wet. With hard steels there is less danger of scratching the surface during polishing, and a plentiful supply of polishing powder should be used. In the grinding operations very great care is required to prevent heating of the specimen which may affect the structure.

Etching.—A 1/or 2 per cent. solution of nitric acid in alcohol or a 5 per cent. solution of picric acid in alcohol.

The time of etching varies because the rate of attack depends very largely on the condition of the steel as regards tempering. Troostitic steels on etching become covered with a velvety deposit of carbon. It is advisable to remove this by lightly rubbing on a pad, and to re-etch for about 2 seconds, when a sharper structure is obtained. A light repolishing and re-etching is often advantageous in revealing the structure of sorbitic and other steels.

Detection of Regions of Local Hardening.—Clean and roughly polish the surface of the steel with emery paper. Immerse in 5 per cent. aqueous or 10 per cent. alcoholic solution of nitric acid for 2 minutes, wipe off the deposit,

and immerse again; wash with water, and dry with alcohol or acetone, without wiping. The line of demarcation between hardened and unhardened regions is clearly visible, the former being blackened and the latter etched dull grey. The black deposit takes some time to form on a fully hardened steel, but shows most quickly on a slightly tempered steel. The second etching generally gives a sharper result, and a better contrast can also be obtained by adding a little ammonium persulphate to the solution.

CHAPTER IX

THE STRUCTURE AND PROPERTIES OF ALLOY STEELS, AND THE EFFECT OF HEAT TREATMENT

SPECIAL elements are intentionally added to carbon steels in order to modify their physical, chemical or mechanical properties and render them suitable for special purposes.

The same structural constituents are found in alloy steels as in carbon steel, but their composition is modified by the presence of the alloying element, and their limits of existence, both as regards composition and temperature, are affected by the modification of the critical range which the alloying element introduces. They may be classified from the microscopical standpoint according as the most important constituent of the slowly cooled steel is pearlite, martensite, austenite, or free carbide. The structure depends not only on the amount of special element, but on the percentage of carbon present: in the following table the approximate figures given for the limits of composition of the different microstructural groups are based on the work of Guillet.

Principal carbon-containing micro-constituent in the slowly cooled steel.	Nickel Steels.		Manganese Steels.		Chromium Steels.	
	Nickel per cent.		Manganese per cent.		Chromium per cent.	
Percentage of carbon	0·2	0·8	0·2	0·8		0·8
Pearlite . .	0 to 8	0 to 5	0 to 5	0 to 3	0 to 7	0 to 3
Martensite . .	8 „ 26	5 „ 15	5 „ 12	3 „ 7	7 „ 15	3 „ 10
Austenite . .	>26	>15	>12	>7	—	—
Free carbide .					>15	>10

There is no sharp demarcation between the pearlitic and martensitic groups, which merge into one another through the usual transition products, sorbitic pearlite, troostite, etc.

The steels most frequently used are the pearlitic steels containing relatively small amounts of the alloying element but after slow cooling their properties are not remarkably better than those of carbon steels. To get full advantage of the use of the alloying element, they are almost invariably heat-treated. The pearlitic steels are all hardened by quenching, and show similar characteristic types of microstructure to those shown by carbon steels. The constitutional diagrams of many ternary and some more complex systems have been determined but for the pearlitic alloy steels the iron–carbon constitutional diagram may be used provisionally as a guide to heat treatment, provided that allowance is made for the change in critical ranges and account is taken of the accompanying effect of alteration of the eutectoid composition. Steels which after slow cooling are martensitic or show much free carbide are hard and brittle, but some of them after treatment are employed as tool steels. Such steels become austenitic, and their hardness is reduced by quenching, but restored by tempering. Some austenitic steels have important commercial uses: they are softer than martensitic steels and have a low elastic limit; after quenching they remain austenitic, and if originally free from separated carbide are unaffected in hardness.

Nickel Steels.—In the pearlitic steels the nickel passes mainly into solid solution in the ferrite, a small proportion being associated as Ni_3C with the Fe_3C of the cementite. The principal pearlitic nickel steels in commercial use are those containing 0·25 to 0·40 per cent. of carbon, with 3 to 3·75 per cent. of nickel. They are used in the heat-treated condition for crankshafts, axles, connecting rods, etc., as well as for ordnance. Some changes in their structure on heat treatment are illustrated in Figs. 154 to 158. The critical temperatures Ar_3 and Ar_1 are much lower than in carbon steels, and for a given rate of cooling the separation of ferrite and formation of pearlite take place less readily. The presence of 3 per cent. of nickel lowers Ac_1 by over 30° C.

FIG. 153.—Nickel steel, containing carbon 0·16 per cent., manganese 0·54 per cent., and nickel 9·1 per cent., and showing a troosto-martensitic structure after slow cooling.

Etched with 1 per cent. nitric acid in alcohol. × 500.

Heat treatment of a nickel steel containing carbon 0·35 per cent., manganese 0·65 per cent., nickel 3·76 per cent.

Critical points on heating $\begin{cases} Ac_1 \text{ max. } 696^\circ \text{ C.} \\ Ac_3 \text{ ends } 743^\circ \text{ C.} \end{cases}$

All etched with 2 per cent. nitric acid in alcohol. Magnification 250 diameters.

FIG. 154.—Slowly cooled from 900° C. Ferrite network enclosing grains of lamellar pearlite. Brinell hardness 199.

FIG. 155.—The steel of Fig. 154 heated to 692° (Ac_1) and cooled in oil. The ferrite and carbide of the pearlite which have passed into solid solution, are retained as fine martensite on quenching in oil, the ferrite network remaining almost intact. Brinell hardness 250.

FIG. 156.—The steel of Fig. 154 heated to 900° C. and quenched in water. A uniform solid solution having been obtained above Ac_3 the structure is wholly martensitic on quenching. Brinell hardness 484.

FIG. 157.—The steel of Fig. 156 heated for 2 hours at 630° C. The martensite has broken down to form sorbite or fine coalesced carbide in a groundmass of ferrite. Brinell hardness 242. Although the hardness of this structure is similar to that of the structure shown in Fig. 155, its yield point and impact figure are very much higher.

FIG. 158.—The steel of Fig. 157 heated to 743° C. (end of Ac_3) and cooled slowly. The structure has reverted to ferrite and lamellar pearlite, only differing from the original (Fig. 154) in grain size. Brinell hardness 196.

FIG. 153.

FIG. 154.

FIG. 155.

FIG. 156.

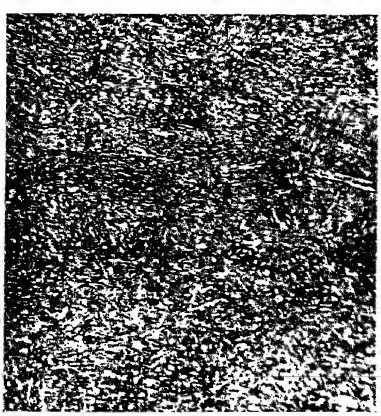


FIG. 157.

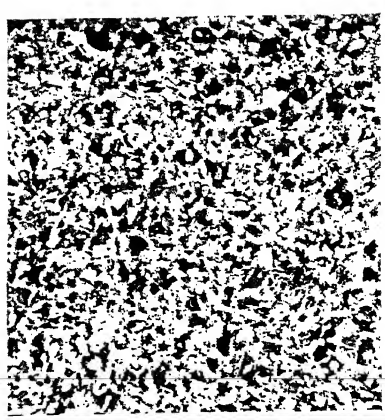


FIG. 158.

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PLATE XXX.

FIG. 159.

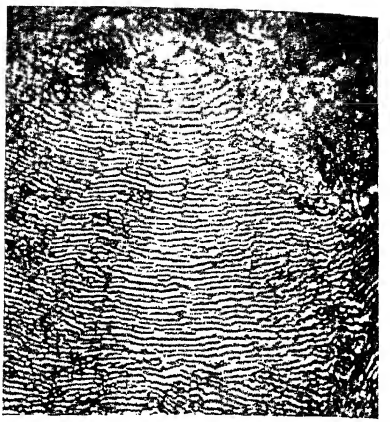
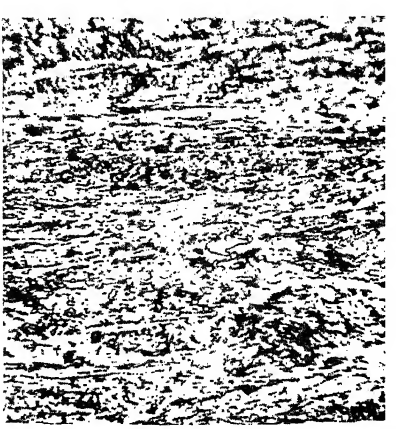


FIG. 160.

FIG. 161.

FIG. 162.



Alloy steels.

All etched with 1 per cent. nitric acid in alcohol.

FIG. 159.—Steel containing carbon 0·43 per cent., chromium 3·0 per cent., air-cooled from 900° C. Troosto-martensite. Brinell hardness 372. × 250.

FIG. 160.—The same steel as in Fig. 159 slowly cooled from 900° C. (cooled through the critical range at 0·7° C. per minute). Pearlite. Brinell hardness 180. × 1000.

FIG. 161.—Low-carbon nickel–chromium steel forging (carbon 0·2 per cent., nickel 3·5 per cent., chromium 0·6 per cent.), oil-hardened and tempered. Fine coalesced carbide in a groundmass of ferrite, the arrangement of the carbide preserving the appearance of the martensite in the hardened steel. × 250.

FIG. 162.—Nickel–chromium–molybdenum steel forging (carbon 0·25, nickel 2·6, chromium 0·9, molybdenum 0·55 per cent.), oil-hardened and tempered. Sorbite.

The hardening temperature has been high, hence the large grain size, but the mechanical properties did not apparently suffer much deterioration on that account. × 1000.

FIG. 163.—Medium-carbon nickel–chromium steel (carbon 0·31 per cent., nickel 3·62 per cent., chromium 0·82 per cent.), slowly cooled from 900° C. Ferrite and sorbitic pearlite. × 100.

FIG. 164.—Cold-drawn chromium–vanadium steel (carbon 0·42 per cent., chromium 1·11 per cent., vanadium 0·20 per cent.). Tensile strength 107 tons per sq. inch. The original structure before drawing was fine coalesced carbide in a groundmass of ferrite: the carbide particles remain in the severely deformed groundmass.

There is no change in the appearance of the micro-structure on annealing at temperatures of 250° to 300° C., a treatment which improves the elastic properties but impairs the ductility. On annealing above 300° C. softening sets in, but the micro-structure is not visibly affected until an annealing temperature of 500° C. to 600° C. is reached, when softening becomes very rapid and is accompanied by recrystallisation of the ferrite and coalescence of the carbide. × 1000.

and the maximum tempering temperature which may safely be applied must be correspondingly lower than that permissible for carbon steel (see p. 131). The Ac_3 point is lowered still more and a lower hardening temperature than for carbon steel is permissible. On the other hand, there is a wider range of hardening temperatures above Ac_3, resulting in no deterioration in properties, so that there is no danger in exceeding Ac_3 by a good margin. Three per cent. of nickel reduces the carbon content of the eutectoid to about 0·75 per cent., but a nickel steel containing such high carbon readily deposits graphite during annealing or hot rolling, and chromium or manganese must be added to keep the carbon in the combined state.

Nickel steels containing about 0·1 per cent. of carbon, and 2 to 5 per cent. of nickel are used for case hardening. If the surface of a 5 per cent. nickel steel is carburised to about 0·9 per cent. of carbon it will be martensitic after comparatively slow cooling; and a structure is thus produced to obtain which carburising and quenching would be necessary in a case-hardened mild steel. A 2 per cent. nickel steel similarly carburised and slowly cooled would be troostitic. Fig. 153 shows a steel containing 9·1 per cent. of nickel and 0·16 per cent. of carbon, very slowly cooled, and illustrates the structure of the martensitic steels.

Of the other nickel steels, the austenitic steels (Fig. 128), containing 25 to 35 per cent. of nickel with about 0·2 per cent. of carbon, have been used for gas-engine valves, turbine blading, etc.; those containing 36 per cent. of nickel with low carbon (known as "invar" on account of their exceedingly small coefficient of dilatation between 0° and 350° C.) are used for clocks, geodetic and similar instruments, etc.

Manganese Steels.—All commercial steels contain manganese, added to reduce oxides and to counteract the harmful influence of sulphide of iron by converting the sulphur into the comparatively harmless manganese sulphide. Any manganese in excess partly passes into solution in the iron, and

partly combines with the carbon to give Mn_3C, which occurs in association with Fe_3C in the cementite.

Manganese lowers the critical ranges Ar_3 and Ar_1 in a marked degree. A small quantity of manganese tends to suppress the formation of pearlite; typical manganiferous pearlite is sorbitic (Fig. 100), and of high tensile strength.

Pearlitic manganese steels are used as structural steels (p. 119), and steels with 1·5 to 2·0 per cent. manganese have excellent properties when suitably heat-treated (Figs. 165, 166). Fig. 169 illustrates the structure of slowly cooled manganese steels of the martensitic class, which are of no industrial importance between 5 and 12 per cent. of manganese.

The important commercial manganese steel is Hadfield's, containing 12 to 14 per cent. of manganese, and about 1·5 per cent. of carbon. It is used for railway points and crossings, rock drills, stone crushers, armour, etc.; it possesses great resistance to wear and is austenitic in structure as used in the water-quenched condition, but any deformation undergone hardens the steel by the formation of martensite. In this, as in some other austenitic steels in which martensite or free carbide may be formed on slow cooling, such a change is suppressed and the properties improved by water-toughening, *i.e.* heating to 1000° C. and quenching in water (Fig. 170).

Chromium Steels.—The chromium in pearlitic steel occurs partly in solution in the ferrite, but chiefly as carbide of chromium, Cr_3C_2, which replaces Fe_3C. With higher percentages of chromium a definite double carbide of Fe_3C and Cr_4C probably exists. Chromium raises the critical range (Ac_1 and Ac_3) on heating: the Ac_2 point is unchanged. It first lowers Ar_3, but raises Ar_1 while at the same time tending to prevent the formation of pearlite on cooling. Chromium steels are very sensitive to rate of cooling; a small increase in the rate may cause almost entire suppression of the formation of pearlite. The maximum temperature from which cooling takes place has also a marked

effect, and this is especially so for steels with high chromium content. A high initial temperature, like a quick rate of cooling, tends to lower the temperature of Ar_1, and to suppress more completely the formation of pearlite. Small quantities of chromium (0·5 to 1·0 per cent.) improve the properties of heat-treated carbon steels, and diminish the rate at which tempering occurs. Such steels with 0·55 to 0·65 per cent. carbon are used for automobile springs and gear wheels, and with higher carbon for tools such as axes, chisels, files, etc. Ball bearings are made from steels containing 1·25 to 1·75 per cent. of chromium and 1 per cent. of carbon. These and other hyper-eutectoid chromium steels should receive a preliminary treatment before hardening to dissolve massive carbide and precipitate it in a finely divided form, so putting it into a condition in which solution readily occurs at the hardening temperature. Steels with 2 per cent. chromium and 0·8 to 1·8 per cent. carbon are intensely hard after treatment, and have been used for rock crushers, and also, welded in alternate layers with wrought iron, for safes. Steel with 3 per cent. chromium is shown in Figs. 159, 160. Corrosion- and heat-resisting steels containing chromium are dealt with in a later section.

Nickel–Chromium Steels.—A great variety of these steels has been used for automobile and aeroplane parts, and also for guns, projectiles and armour plate. All such steels are pearlitic in the slowly cooled condition. The important commercial nickel–chromium steels and some of their uses are indicated in the table on page 146. Structures of the steel containing about 3·5 per cent. of nickel and 0·5 per cent. chromium are shown in Figs. 161, 163, 175, 176. In this steel, Ac_1 occurs at about 720° C. The position of Ar_1 depends on the initial temperature and the rate of cooling. Broadly speaking, if the steel is cooled fairly slowly from a temperature just above Ac_3 the carbide change occurs at about 600° C., while with the same rate of cooling from a higher initial temperature the change at 600° (Ar′) will be

first partially and (as the initial temperature rises) almost totally suppressed and will be completed at 460° (Ar″). Air-cooling has a pronounced effect on most nickel–chromium steels in lowering the change point and suppressing the formation of pearlite with consequent partial hardening.

The true air-hardening steels are martensitic after air-cooling: their properties (especially as regards impact figure) are considerably improved without much loss of hardness, and with no change in microstructure, by tempering at 300° after air-hardening, or they may be tempered at 600° to 650° C. giving uniform sorbitic structures without free ferrite, and properties similar to those of oil-hardened and tempered nickel–chromium steel of lower chromium content.

Molybdenum Steels.—Carbon–molybdenum steels are rarely used except to secure increased strength at raised temperatures, but molybdenum is a valuable addition to other alloy steels, one point of interest being the small percentage which effects the maximum improvement. Molybdenum, when present in small quantities in the annealed steel, is partly combined with carbon to form a complex carbide of iron and molybdenum and is partly in solid solution in the ferrite.

The properties of a steel containing about 0·35 to 0·4 per cent. of carbon and 1·6 to 1·8 per cent. of manganese are greatly improved by the addition of 0·2 to 0·3 per cent. of molybdenum (Figs. 165 to 168). The improvement of the properties is associated with the suppression of the separation of ferrite even at moderate rates of cooling.

This effect is the result of the marked lowering of the critical range on cooling which is a characteristic effect of the addition of molybdenum. For example, in nickel–chromium–molybdenum steels the Ar point can only be induced to occur at the upper or Ar′ position (about 600° C.) when cooling is very slow indeed. With ordinary slow cooling, it occurs wholly at Ar″ (460° C.).

Of all the steels containing molybdenum, the nickel–

NICKEL–CHROMIUM STEELS.

Type.	Composition.				Mechanical Tests.					Uses.
	Carbon per cent.	Manganese per cent.	Nickel per cent.	Chromium per cent.	Yield point. Tons per sq. in.	Maximum Load. Tons per sq. in.	Elongation per cent. on 2 in.	Reduction of area per cent.	Izod Impact Figure. Ft.-lbs.	
2 per cent. nickel.					Min.		Min.	Min.	Min.	
Medium low-chromium.	0·3 to 0·4	0·3 to 0·6	1·5 to 2·5	0·5 to 1·0	30	40–45	25	50	50	Automobile axles and crankshafts.
Medium high-chromium.				1·0 to 1·7	40	55–65	18	35	20	Ordnance, armour.
3½ per cent. nickel.										
Mild.	0·15 to 0·25				40	50–60	19	55	40	Automobile crankshafts, heavy lorry crankshafts and axles, ordnance, armour.
Medium.	0·25 to 0·35	0·25 to 0·55	3·25 to 4·0	0·4 to 0·8	45	55–65	18	50	35	Automobile and aero engines, crankshafts, spindles, propeller shafts, axles, connecting rods.
Hard.	0·3 to 0·4				50	60–70	17	40	25	As above for highly stressed parts.
Air-hardening nickel–chromium steel.										
Air-hardened.	0·25 to 0·35	0·35 to 0·55	3·5 to 4·25	1·0 to 1·5	75	100–125	8	20	8	Gearwheels, connecting rods, propeller shafts for motor-boats.
The same tempered at 600°.					45	55–65	15	45	35	

Note.—The results of tests given are approximately those obtained with longitudinal test-pieces cut from bars, treated (except where otherwise stated) by oil-hardening and tempering at 600° C. Transverse tests on large forgings or plate give lower results.

STRUCTURE AND PROPERTIES OF HEAT-TREATED FORGINGS.

Type of steel and treatment.	Composition.				Mechanical Tests.						Micrograph.
	Carbon per cent.	Manganese per cent.	Nickel per cent.	Chromium per cent.	Elastic Limit. Tons per sq. in.	Yield point. Tons per sq. in.	Maximum Load. Tons per sq. in.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Izod Impact Figure. Ft.-lbs.	
Carbon steel.											
Medium-sized forging quenched in oil and tempered . .	0·34	0·68	—	—	15	18·0	35·0	30	54	16	Fig. 171.
Similar forging (from same cast of steel) quenched in water and tempered .	0·34	0·68	—	—	18	24·8	39·5	20	42	15	Fig. 172.
Nickel steel.											
Large forging, oil-hardened and tempered . . .	0·37	0·61	3·55	—	24	28	44·8	22	45	18	Fig. 173.
Small forging, oil-hardened and tempered . . .	0·36	0·55	3·65	—	29	32	46·0	20	30	26	Fig. 174.
Nickel–chromium steel.											
Large forging, oil-hardened and tempered . . .	0·28	0·40	3·59	0·51	27	32·7	43·6	21·5	53	32	Fig. 175.
Small forging, oil-hardened and tempered . . .	0·26	0·66	3·53	0·84	31	38·8	48·7	21	56	59	Fig. 176.

Note.—Hardening temperature of large nickel steel forging rather high, otherwise temperatures of treatment approximately the same throughout. Wall thickness of small forgings 2 ins., of large forgings over 4 ins. All tests taken transversely to the direction of forging.

chromium–molybdenum steels provide the best all-round combination of properties, and are extensively used for crankshafts, gears, dies for drop stampings, die-casting moulds, forgings and stampings for general engineering purposes. They find their most important applications where the use of large masses of metal are involved, *e.g.* for ordnance, turbine rotors and rotor discs (Figs. 162, 183, 184).

In addition both nickel and chromium steels containing molybdenum are widely used. Chromium–molybdenum steels containing 3 per cent. of chromium and 0·6 per cent. of molybdenum show a very good combination and range of properties for constructional engineering purposes: with 6 per cent. of chromium and 0·4 per cent. of molybdenum they are used for chemical high-pressure vessels. Chromium–molybdenum steels are distinguished by a high notched-bar impact figure, though the elastic limit and yield point are slightly lower than those of nickel–chromium–molybdenum steels of the same hardness. Nickel–molybdenum steels, on the other hand, show higher yield ratios with considerably lower impact figures than nickel–chromium–molybdenum steels, and when their tensile strength exceeds 60 tons per square inch they are more difficult to machine than chromium– or nickel–chromium–molybdenum steels of the same hardness.

Vanadium Steels.—In the pearlitic steels vanadium replaces iron in the cementite which, when the vanadium content reaches 5 per cent., consists entirely of V_4C_3. Vanadium has a powerful effect on the mechanical properties of steel, and apart from its use in tool steel which may contain as much as 2·5 per cent. of vanadium, it is rarely added in amounts exceeding 0·5 per cent.

Carbon–vanadium steels containing carbon 0·5 per cent., vanadium 0·2 per cent., are occasionally used, but the most commonly employed vanadium steel is chromium–vanadium steel used for case-hardened parts, such as gears, for small stampings and forgings, and with a higher carbon content, for springs.

Nickel–vanadium steels are rarely used, but nickel–chromium–vanadium steels containing 0·1 to 0·3 per cent. of vanadium are sometimes employed to replace nickel–chromium steels, which they closely resemble in properties.

The effect of tempering on steels containing vanadium hardened in sections of small or moderate size differs from that of the corresponding steels without vanadium in that the regular fall in hardness is interrupted at temperatures between 500° and 600° C., though it sets in at an increased rate on tempering at higher temperatures. Thus, improved regularity of properties in routine tests can be achieved if the composition of the steel is so adjusted as to make the required tests correspond to the flat part of the tempering curve.

The microstructure does not give any indication as to whether tempering has been carried out at or above this temperature range. Approximately constant hardness in spite of increasing tempering temperature appears to be the result of a superimposed temper-hardening effect due to the decomposition of a supersaturated solution of vanadium carbide in α-iron, probably formed by rapid cooling of the γ solid solution.

Use of Alloy Steels to increase the Efficiency of Hardening of Large Masses.—An advantage of the use of alloy steels is that they enable mechanical properties of a high order to be obtained, by heat treatment, in large masses of steel. With large masses of carbon steel it is impossible to obtain, by oil-quenching, or even by water-quenching, a sufficiently fast rate of cooling to prevent the formation of a structure of ferrite and pearlite; but the addition of special elements which lower the critical range on cooling or suppress the separation of ferrite enables a slower rate of cooling to be successfully employed. The table on page 147 illustrates the partial compensation of the effect of mass, (1) by more rapid quenching of carbon steel, (2) by the use of a nickel steel in which, however, the effect is still pronounced, but

Effect of mass in the heat treatment of steels containing manganese, and the influence of molybdenum in reducing this effect.

Steels oil-hardened from 840° C.; tempered at 550° C. and cooled in air.

FIG. 165.—Carbon 0·35 per cent., manganese 1·34 per cent.: ¾-inch diameter bar.

FIG. 166.—The same steel: centre of 2½-inch diameter bar.

FIG. 167.—Carbon 0·38 per cent., manganese 1·42 per cent., molybdenum 0·23 per cent.: ¾-inch diameter bar.

FIG. 168.—The same steel: centre of 2½-inch diameter bar.

All etched with 2 per cent. nitric acid in alcohol. × 250.

Mechanical Properties associated with the Structures illustrated.

	Fig. 165.	Fig. 166.	Fig. 167.	Fig. 168.
Elastic limit, tons per sq. in..	37	23	55	31
Yield point, tons per sq. in. .	44·4	26·8	60·4	37·4
Maximum load, tons per sq. in.	55·0	43·8	68·1	50·9
Ratio of yield point to max. load	0·81	0·61	0·89	0·74
Elongation per cent. on 2 ins.	21	25	19	22
Reduction of area per cent. .	58	58	55	57
Izod impact figure, ft.-lbs. .	73	26	57	31
Brinell hardness number .	254	220	327	242

FIG. 169.—Steel containing carbon 0·4 per cent., manganese 5·0 per cent. slowly cooled from 900° C. Martensite. Brinell hardness 530.

Etched with 1 per cent. nitric acid in alcohol. × 250.

FIG. 170.—Manganese steel (carbon 1·2 per cent., manganese 13·2 per cent.) quenched in water from 1000° C. Austenite, showing twinning.

Yield point . . 21 tons per sq. inch.
Tensile strength . . 60 ,, ,,
Elongation . . 70 per cent. on 2 inches.

Brinell hardness 210. The steel hardens very rapidly under the influence of any kind of deformation owing to the formation of martensite.

Etched with nitric acid in alcohol. × 50.

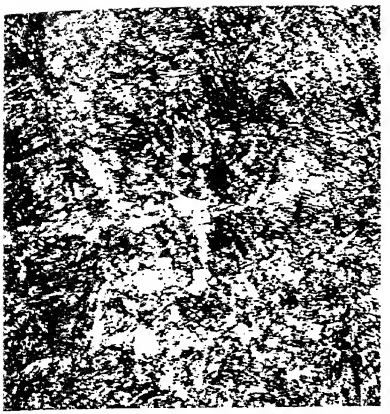


FIG. 165.

FIG. 166.

FIG. 167.

FIG. 168.

FIG. 169.

FIG. 170.

[Facing p. 150

PLATE XXXII.

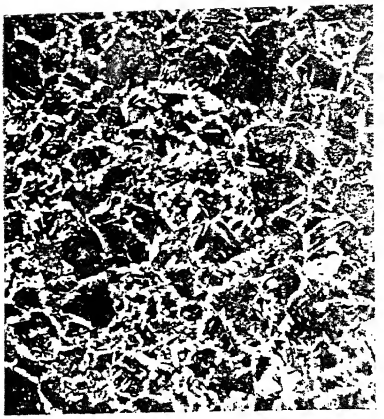


FIG. 171.

FIG. 172.

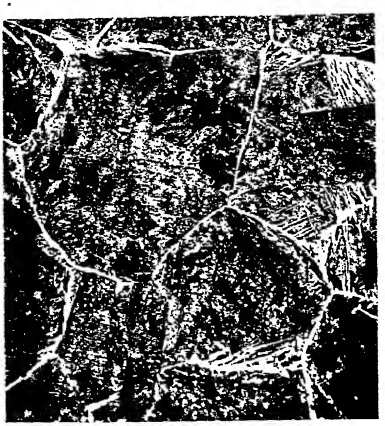


FIG. 173.

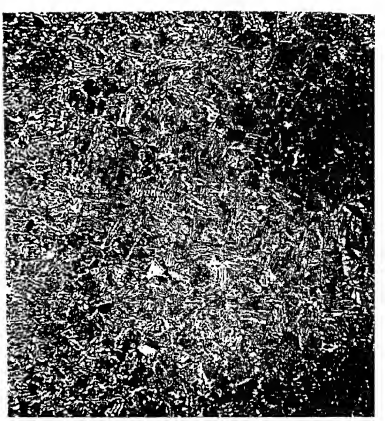
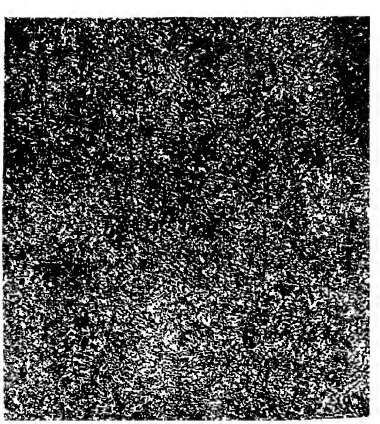


FIG. 174.



Structures of heat-treated forgings referred to in Table on page 147.

All etched with 1 per cent. nitric acid in alcohol. Magnification 100 diameters.

FIG. 171.—Carbon steel forging, oil-hardened and tempered, showing a ferrite network enclosing grains of sorbite.

FIG. 172.—Similar forging, water-hardened and tempered, showing decrease in the amount of free ferrite.

FIG. 173.—Large nickel steel forging, oil-hardened and tempered. Ferrite network enclosing grains of sorbite.

FIG. 174.—Small nickel steel forging, oil-hardened and tempered. Sorbite, with slight separation of free ferrite.

FIG. 175.—Large nickel–chromium steel forging, oil-hardened and tempered. Sorbite with some separation of ferrite.

FIG. 176.—Small nickel–chromium steel forging, oil-hardened and tempered. Uniform sorbite.

Effect of rate of cooling on the position of the austenite transformation and on the structure.

Ar′, Ar″ and Ar‴ refer to the successive positions of the austenite transformation (*i.e.* the Ar_1 point) as the rate of cooling is increased.

Ar′ occurs at 690–550° C. according to composition and rate of cooling and the austenite changes either to pearlite, sorbitic pearlite or troostite according to the temperature of transformation within the Ar′ range.

Ar″ occurs at about 450° C. when the austenite breaks down giving an acicular structure resembling martensite but not so hard.

Ar‴ occurs at 300° C. and below according to composition when the austenite transforms to martensite.

In carbon steel the transformation occurs either at Ar′ or at Ar‴ but not at intermediate temperatures. The change at Ar″ is characteristic of alloy steels, especially those containing chromium, molybdenum, tungsten or vanadium.

still better (3) by employing a nickel–chromium steel of suitable composition.

The properties of very large forgings can only be substantially improved by heat treatment when an alloy steel is used in which hardening is secured at the comparatively slow rates of cooling which are characteristic of the centre of a large mass of steel, quenched in oil.

If the average rate of cooling of the forging is near to the "critical rate of cooling" of the steel, that is, to the rate of cooling which will just produce efficient hardening, the material adjacent to the surface and to the ends is hardened much more than that at the centre, and the difference in properties persists, though to a reduced extent, after tempering.

If hardening is inefficient, so that no part is properly hardened, or if it is quite efficient, so that the forging is hardened throughout, the variation in properties from place to place in the forging after tempering is small; but in the first instance the ratio of yield point to tensile strength is low and in the second instance it is high.

Of the steels given in the table on page 154 it will be seen that the nickel–chromium–molybdenum steel was most uniform in properties. A comparison of the microstructures (Figs. 177 to 184) will show that the nickel–chromium–molybdenum steel forging was uniformly sorbitic throughout, but examination of the wall of the other forgings showed more ferrite at the centre than at the outside, though on account of the large separation of ferrite at the outside of the nickel steel forging the difference in structure was only slight.

Use of Alloy Steels to increase the Stability of the Hardened Condition at High Temperatures.—Only carbon steels (usually containing over 0·9 per cent. of carbon) were used for cutting purposes up to the time of the discovery of the properties of tungsten steel by Mushet. Mushet's steel contained about 5 per cent. of tungsten, over 2 per cent. of carbon with high manganese and silicon, and had the property of self-hardening (*i.e.* the martensitic condition was

retained after comparatively slow cooling in air). Hardened alloy steels in general do not soften so readily on tempering as carbon steels, and tungsten steel exhibits the property of retaining its hardness to a marked degree. Hence tools of this material were found to work at higher speeds than carbon tool-steel without damage due to heating.

Tool-steels were still further improved about 1900 by increasing the tungsten content to about 8 per cent. and adding about 4 per cent. of chromium; and later, modern high-speed tool-steels were introduced containing, on an average, carbon 0·6 to 0·7 per cent., tungsten 12 to 18 per cent., chromium 3 to 4 per cent., vanadium 0·25 to 1·0 per cent. These are hardened by heating to about 1300° C. and cooling in air. The soft steel (slowly cooled from 800° C.) consists of globules of carbide in a groundmass of sorbitic pearlite; the hardened steel shows a martensite-austenite mixture enclosed in austenitic grains. Whereas hardened carbon steel is appreciably softened by heating, say, to 250° C., and rapidly loses its hardness at higher temperatures, these high chromium–tungsten steels show no progressive softening until the temperature reaches about 700° C. As the tempering temperature is raised from 300° to 650° C. they actually become harder, the austenite being converted into martensite. Heating to about 600° C. therefore constitutes a secondary hardening.

Corrosion- and Heat-resisting Steels.—Stainless steel for cutlery contains about 12·5 to 14·5 per cent. of chromium and 0·3 to 0·4 per cent. of carbon. On account of the raising of the critical range, already referred to as an effect of chromium, it requires hardening from a temperature of 950° to 1000° C. Knife-blades are often quenched in an oil-bath at about 180° to 200° C., or tempered at a similar temperature after quenching to give a Brinell hardness of about 550, or a tensile strength of about 110 tons per sq. inch.

For general engineering purposes such as turbine blades, pump rods, valves and machinery parts, a similar steel con-

Structure and properties of large heat-treated forgings.
Wall thickness, 8 inches.

All etched with 2 per cent. nitric acid in alcohol.
Magnification 250 diameters.

Nickel steel.

FIG. 177.—Near outside surface. Ferrite and sorbitic pearlite.

FIG. 178.—Middle of wall. Increased separation of ferrite.

Nickel steel containing 0·26 per cent. chromium.

FIG. 179.—Near outside surface. Mainly sorbite.

FIG. 180.—Middle of wall. Ferrite and sorbite.

Nickel–chromium steel.

FIG. 181.—Near outside surface. Mainly sorbite.

FIG. 182.—Middle of wall. Increased separation of ferrite.

Nickel–chromium–molybdenum steel.

FIG. 183.—Near outside surface } Uniform sorbite.
FIG. 184.—Middle of wall. }

STRUCTURE AND PROPERTIES OF LARGE HEAT-TREATED FORGINGS (a) NEAR OUTSIDE SURFACE; (b) AT MIDDLE OF 8-INCH WALL.

Type of steel and treatment.	Composition.					Mechanical tests.						Micrograph.
	Carbon, per cent.	Manganese, per cent.	Nickel, per cent.	Chromium, per cent.	Molybdenum, per cent.	Elastic limit, tons per sq. in.	Yield point, tons per sq. in.	Maximum load, tons per sq. in.	Elongation, per cent. on 2 inches.	Reduction of area, per cent.	Izod impact figure, ft.-lbs.	
Nickel O.H. 850°, T. 460°	0·33	0·66	3·82	Tr.	Nil	(a) 27	31·5	48·2	19	37	20	Fig. 177
						(b) 24	29·4	45·7	21	41	28	Fig. 178
Nickel O.H. 835°, T. 540°	0·38	0·74	3·47	0·26	Nil	(a) 35	43·0	55·1	17	43	15	Fig. 179
						(b) 29	36·9	48·7	16	39	16	Fig. 180
Nickel–chromium O.H. 850°, T. 620°	0·28	0·37	3·62	0·67	Nil	(a) 34	37·4	46·5	17	39	21	Fig. 181
						(b) 29	33·0	43·9	19	43	36	Fig. 182
Nickel–chromium–molybdenum O.H. 835°, T. 650°	0·29	0·48	2·47	0·64	0·47	(a) 37	41·7	51·9	19	49	31	Fig. 183
						(b) 37	41·7	51·9	19	49	29	Fig. 184

In very large forgings of carbon or nickel steels when the rate of cooling is not sufficient to depress the transformation to Ar‴ (the martensite point) there is separation of ferrite in the form of a network and decomposition of the austenite occurs at Ar′ (see page 151) giving pearlite, sorbitic pearlite, or troostite which is subsequently tempered to sorbite (see table on page 124).

In very large forgings of nickel–chromium and nickel–chromium–molybdenum steels, when the rate of cooling is not sufficient to depress the transformation to Ar‴, most of the change will occur at the intermediate position Ar″ giving an acicular microstructure which persists on tempering.

In this connection see W. T. Griffiths, L. B. Pfeil and N. P. Allen, "The Intermediate Transformation in Alloy Steels," *Iron and Steel Institute, Second Alloy Steels Report*, 1939, p. 343.

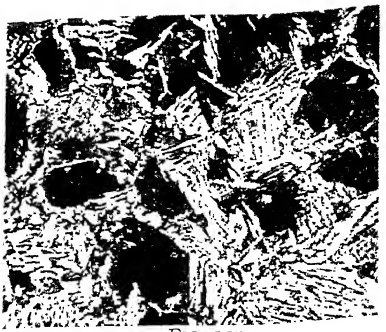


FIG. 177.

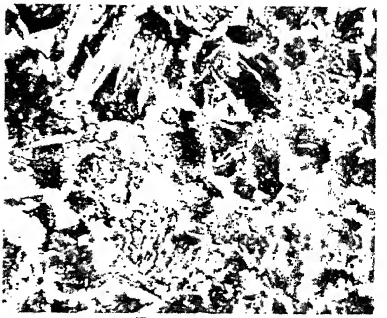


FIG. 178.

FIG. 179.

FIG. 180.

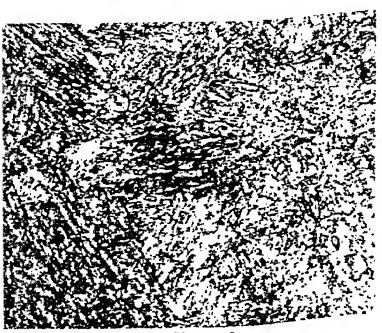


FIG. 181.

FIG. 182.

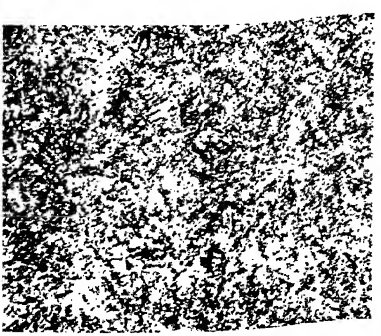


FIG. 183.

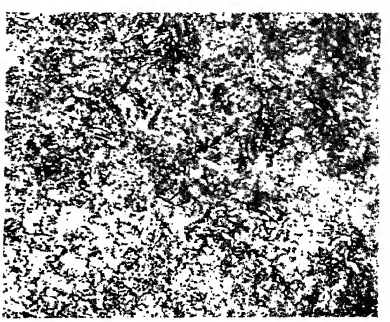


FIG. 184.

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PLATE XXXIV.

FIG. 185.

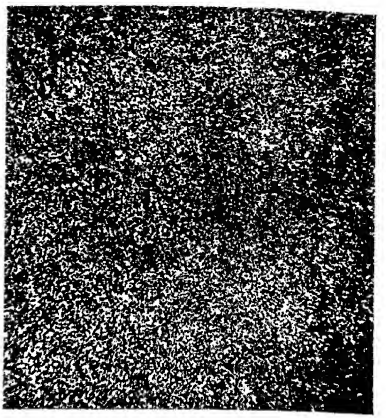


FIG. 186.

FIG. 187.

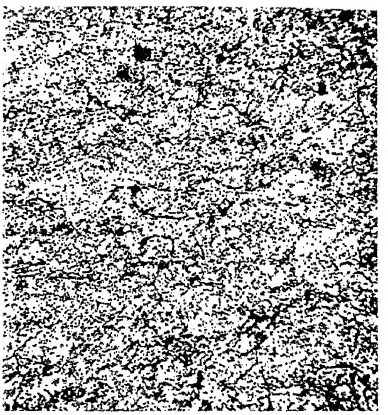
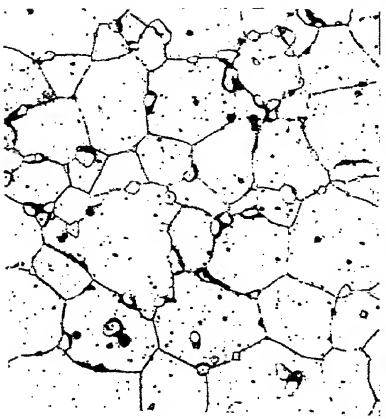
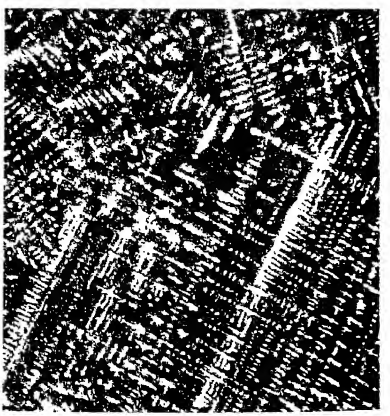


FIG. 188.





All (except Fig. 190) etched with 10 per cent. ammonium persulphate in 10 per cent. hydrochloric acid.

FIG. 185.—Low-carbon stainless steel (carbon 0·18 per cent.. chromium 13 per cent.) air-hardened from 1000° C., reheated to 750° C. and slowly cooled.

After this treatment the steel is in the soft condition consisting of globules of carbide in a groundmass of chromiferous ferrite. × 1000.

FIG. 186.—Stainless steel containing carbon 0·35 per cent. and chromium 13·5 per cent., oil-hardened and tempered. Sorbite. × 250.

FIG. 187.—Austenitic stainless steel (carbon 0·15 per cent., nickel 7·8 per cent., chromium 19·8 per cent.), rolled, annealed at 1000° C. and cooled in air, showing twinning of the γ-iron solid solution. × 50.

FIG. 188.—Austenitic stainless and heat-resisting steel (carbon 0·43, manganese 1·57, nickel 36·2, chromium 11·0 per cent.), water-quenched from 1000° C. and reheated at 700° C. After water-quenching the steel consists of polyhedral grains of austenite: reheating causes a uniform precipitation of carbide which reduces elongation and notched-bar impact figure, but increases the hardness and tensile strength, in particular the strength at high temperatures. × 250

FIG. 189.—Chromium–iron alloy (carbon 0·2 per cent., chromium 28 per cent.), heated to 1000° and cooled in air, consisting of large grains of chromiferous ferrite and coalesced particles of carbide. × 100.

FIG. 190.—Stellite. The composition of stellite varies: the original material contained cobalt 75 per cent., chromium 25 per cent. The specimen shown contains cobalt 45 per cent., chromium 30 per cent., tungsten 20 per cent., and other elements 5 per cent. The dendritic structure of the cast alloy is not modified, nor is the hardness affected by heat treatment at temperatures up to 1150° C. Crushing strength, 135 tons per sq. inch. Etched with aqua regia. × 100.

Mechanical Properties associated with the Structures illustrated.

	Fig. 185.	Fig. 186.	Fig. 187.	Fig. 189.
Yield point, tons per sq. in.	35	46	13	20
Maximum load, tons per sq. in.	42	54	43	36
Elongation, per cent. on 2 ins.	30	20	50	30
Reduction of area, per cent.	65	50	60	50
Izod impact figure, ft.-lbs.	120	27	115	2
Brinell hardness number	198	245	160	155

taining as a rule not more than 0·3 per cent. of carbon is used. The hardened steel may be tempered at temperatures between 550° and 700° C. to give a sorbitic structure (Fig. 186), and a wide range of mechanical properties may be obtained by varying the composition and heat treatment. Thus, a low-carbon corrosion-resisting steel, commercially known as stainless iron, contains about 12 per cent. of chromium and under 0·1 per cent. of carbon, and when heat-treated develops less strength but greater ductility than ordinary stainless steel. Its structure as treated is often identical with that of the steels containing higher carbon, though if its hardening temperature has not been sufficiently high it may contain free chromiferous ferrite. With 12 per cent. of chromium the carbon content of the eutectoid is only 0·3 per cent., so that heat-treated steels with higher carbon tend to show free carbide, and those with lower carbon, free ferrite if complete solution is not attained before quenching. It can be worked more readily than the steel with 0·3 per cent. carbon, and its lower carbon content makes it more resistant to some corrosive influences. It might therefore have a wide application except for the fact that, when great strength is not required, materials of far greater resistance are available in the austenitic corrosion-resisting steels.

Resistance to corrosion increases with the chromium content. It is therefore desirable for chromium to be as high as possible. When chromium reaches about 12 per cent. in the pure carbon-free chromium–iron alloy and about 18 per cent. in the alloy containing 0·25 per cent. carbon, the transformation of α to γ on heating ceases to take place and the alloy becomes unhardenable. In the presence of 2 per cent. of nickel the possibility of obtaining martensite on quenching is restored, but in a steel containing carbon 0·25, chromium 18 and nickel 2 per cent. tempering will not reduce the Brinell hardness to less than 240. Thus the 18 per cent. chromium steel has the highest resistance to corrosion obtainable in a heat-treatable steel. The addition

of more than 2 per cent. of nickel results in steels containing more and more austenite after quenching and a more stable martensitic structure after tempering (with consequent hardness and brittleness), until with 8 per cent. of nickel the change in the constitution of the steels is complete and they then consist of stable austenite unaffected by heat treatment.

The 18 : 8 chromium–nickel type of steel (Fig. 187) has very great advantages in exhibiting a high resistance to corrosion, coupled with a capacity for welding, hot-pressing and undergoing a considerable amount of cold-working; and such steels are therefore widely used for all kinds of corrosion-resisting fittings, chemical plant and domestic ware. They all possess a very low elastic limit and yield point, and their inferior strength cannot be improved by heat treatment, though it can be increased to a marked degree by cold-work followed by tempering. As regards corrosion resistance, the temperature of this tempering is of great importance. If an 18 : 8 chromium–nickel steel is heated within the range 500° to 700° C. precipitation of carbide occurs in the grain boundaries and it becomes liable to intercrystalline attack (Figs. 191, 192). This type of failure is sometimes known as "weld decay," since it was first observed in material adjacent to a weld which had been raised to the dangerous range of temperature during the welding operation.

Reheating to 950° to 1000° C. and air-cooling or quenching will eliminate the defect, but such treatment is frequently inconvenient or impossible to carry out. It is therefore fortunate that the addition of titanium (usually in the presence of tungsten also) has been found very greatly to reduce liability to weld decay, and steels of the 18 : 8 type of modern manufacture contain the necessary additions of these elements, which do not affect the normal structure or properties of the steel.

As a test for susceptibility to this intercrystalline corrosion, strips of steel (about 3 × 1 × $\frac{1}{8}$ inch) may be immersed in a solution of 10 per cent. of copper sulphate and 10 per cent.

of sulphuric acid in distilled water, contained in a flask fitted with a reflux condenser, and maintained at the boiling point for at least 24 hours. Under this treatment pure austenitic grains develop no weakness, but the intergranular films are attacked. The strips are subsequently bent over a radius equal to their own thickness and, in the absence of intergranular attack, should not crack. A steel which will withstand the action of this solution for 72 hours after having first been heated to 650° C. for ½ hour may be regarded as immune from liability to weld decay.

Practical Notes

Polishing.—The usual methods of polishing are employed; grinding must be carried out with great care to avoid heating the specimen. Heating of a thin skin as a result of excessive pressure in grinding, followed by rapid conduction of the heat into the mass of the specimen, may even produce martensitic patches on the surface of some unhardened alloy steels.

Etching.—For pearlitic and martensitic steels of low alloy content the same reagents as for carbon steels are suitable.

Transformer steels containing about 4 per cent. silicon can be etched with 10 per cent. nitric acid in alcohol.

Austenitic manganese steels and some austenitic nickel steels etch readily with 2 per cent. nitric acid in alcohol. Other reagents suitable for austenitic manganese and nickel steels are a 5 per cent. solution of hydrochloric acid (sp. gr. 1·19) in alcohol, a saturated alcoholic solution of picric acid, or an acid solution of ferric chloride containing 5 grams of ferric chloride and 50 c.c. hydrochloric acid in 100 c.c. water.

Stainless steels may be etched with a 10 per cent. solution of hydrochloric acid in alcohol. Its action is slow, the time of etching required being about 5 minutes for the fully softened and 30 minutes for the hardened steel. The reagent specially recommended is an aqueous solution containing 10 per cent.

by volume of concentrated hydrochloric acid and 10 per cent. by weight of ammonium persulphate.* This solution must be freshly made. If the material to be etched is very resistant, a stronger solution may be employed. Aqua regia should not be used, as it causes pitting, and its action, though rapid, is very irregular. A mixture of 1 part of nitric acid and 2 parts of hydrochloric in 2 parts of glycerol gives better results. The specimen should be warmed in hot water before immersion in this etching reagent. It is suitable for high-carbon iron–chromium alloys, and high-speed tool-steel. For low-carbon iron–chromium alloys, nickel–chromium alloys and austenitic steels high in chromium, the amount of hydrochloric acid may be doubled and if necessary a little hydrogen peroxide added.

Free carbide in alloy steels is revealed by etching in alkaline sodium picrate, but its action is slower than on carbon steels and it does not blacken the carbides in chromium or tungsten steels.

For distinguishing carbides in chromium steels an alkaline solution of potassium ferricyanide has been used containing 10 grams of potassium ferricyanide and 10 grams of potassium hydroxide in 100 c.c. water (Murakami's reagent), or the amount of ferricyanide may be doubled (Daeves's reagent). The cold solution etches carbides in chromium steels and tungstides in high-speed tool-steel in about 20 seconds, but about 5 minutes are required in the boiling solution to colour pure cementite (Fe_3C).

* The use in an open room of reagents containing strong acids, and especially those which generate free chlorine, involves risk of damage to instruments and apparatus.

CHAPTER X

NON-METALLIC INCLUSIONS AND DEFECTS IN STEEL

In selecting material from defective steel for microscopical examination it is advisable to make a preliminary examination of as large an area as possible. The structure, immediately visible to the eye, which is shown by sections suitably etched or revealed by contact prints is known as the macrostructure. A description of the usual methods of carrying out the macroscopical examination of iron and steel is given on page 175.

The examination usually includes sulphur printing and macro-etching. Sulphur prints are obtained by applying to the surface of the steel a photographic bromide paper soaked in dilute sulphuric acid. The sulphuric acid liberates sulphuretted hydrogen from the sulphide particles present in the steel, and this reacts with the silver bromide in the immediate vicinity producing dark-coloured spots of silver sulphide. The sulphur print is valuable in that it reveals in a graphic way the uneven distribution of sulphur in the steel, with which is usually associated an uneven distribution of other elements such as phosphorus; but it is not safe to estimate the sulphur content from the density of the print. Thus with the same percentage of sulphur a mild steel (carbon 0·2, manganese 0·3 per cent.) yields a lighter print than a rail steel (carbon 0·5, manganese 1·0 per cent.). Sulphur prints of high-chromium steels may be very misleading if taken as an indication of sulphur content. A stainless steel containing 0·08 per cent. of sulphur and 0·2 per cent. of manganese gives a much fainter print than one containing 0·03 per cent. of sulphur and 0·5 per cent. of manganese.

By etching the surface, both the crystalline character of the

steel and any definite heterogeneity are revealed. Permanent records (macro-prints) of the structure of some steels can be obtained after etching with copper ammonium chloride solutions, the specimen being used as a printing plate. The solution acts by attacking the purer portions which solidified first with greater vigour than it does the impure portions which solidified later. The portions in relief, and thus the darker areas in the prints, therefore, represent the less pure material.

Many defects in steel are traceable to the ingot, and thus one of the most important applications of macroscopical examination is found in the investigation of ingot structures. It is impossible in a short space to deal with so large a subject: reference may be made to the Reports of the Iron and Steel Institute Committee on the Heterogeneity of Steel Ingots by those who have occasion to follow this matter up.*

During the solidification of steel, well-defined dendritic crystals are formed, the outer regions of which are richer in carbon, phosphorus and non-metallic inclusions than the part which solidified first. This dendritic structure exhibits a considerable degree of permanence: it will survive annealing and heat treatment and it is not entirely destroyed by forging.

The ingot shows different types of crystallisation in different parts. At the extreme outside there may be a thin layer of fine crystals; this is succeeded by columnar crystals which have grown out at right angles to the outer surfaces (Fig. 195), while in the central region, where solidification has proceeded more slowly and from numerous centres, equiaxial crystals of irregular orientation are formed (Fig. 196). Forging tends to destroy the primary crystalline structure. When the ingot is forged in a press, however, the columnar crystals may retain their identity in spite of considerable reduction in cross-section (Figs. 198, 199), and they may be a source of weakness on account of the non-metallic inclusions and segregates occurring in the interdendritic regions; but,

* *Journal of the Iron and Steel Institute*, 1926, (1), p. 39; 1928, (1), p. 401; 1929, (1), p. 305, and Special Reports, Nos. 2, 4, 9, 16 and 25.

All (except Fig. 192) etched in 10 per cent. ammonium persulphate in 10 per cent. hydrochloric acid.

FIG. 191.—Radial section of an austenitic steel tube (carbon 0·18 per cent., nickel 10·5 per cent., chromium 16·2 per cent.). The section was taken near a welded flange. The separation of a carbide constituent has occurred at the grain boundaries throughout the wall thickness of the tube, and intergranular corrosion has taken place at the inner surface of the tube which was used for conveying acids.

Carbide in the grain boundaries can be removed by reheating to 1000° C. and cooling rapidly. × 100.

FIG. 192.—Intercrystalline network of cracks at the inner wall of the same tube as shown in Fig. 191.

Unetched. × 50.

FIG. 193.—Cold-rolled austenitic stainless steel (carbon 0·15, nickel 9·9, chromium 16·0, tungsten 1·0 per cent.).

Tensile strength, 76 tons per sq. inch.

Elongation, 6 per cent.

Brinell hardness number, 359.

No change in the microstructure or hardness occurs on heating to 450° C., but the elastic limit is raised by this treatment; above this temperature recrystallisation and softening begin to set in. If, however, the cold, worked steel is heated at temperatures between 550° C. and 900° C., precipitation of carbide occurs both within and around the grains, with consequent risk of intercrystalline corrosion. Hence a steel of this composition cannot be used in the partially softened condition. It must be used in the cold-worked condition (or reheated to not more than 500° C.) or in the softened condition after heating to 1000° C. × 1000.

FIG. 194.—Dendritic structure of the austenitic stainless steel shown in Fig. 191, melted locally by the electric arc. Interdendritic carbide segregation so produced is very persistent, and cannot be removed as easily as the intergranular carbide shown in Fig. 191. × 100.

FIG. 191.

FIG. 192.

FIG. 193.

FIG. 194.

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PLATE. XXXVI.

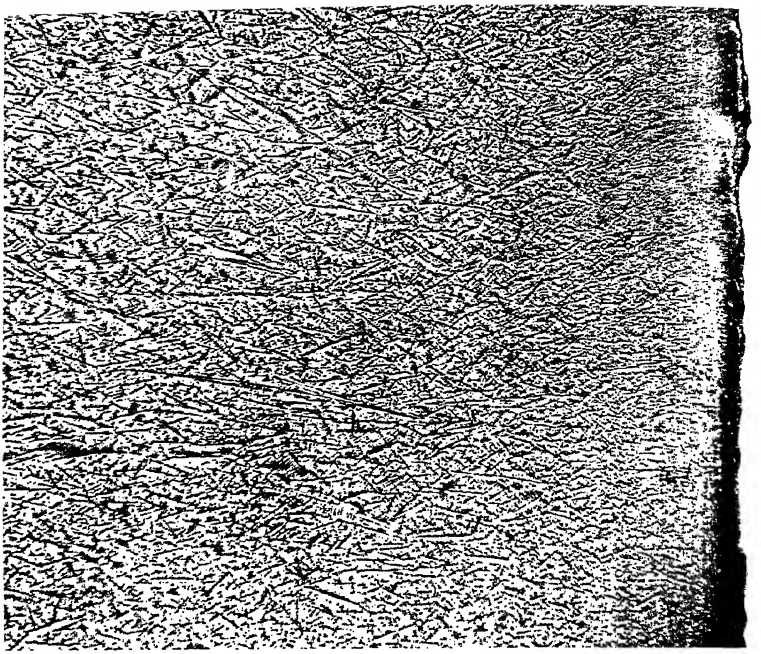
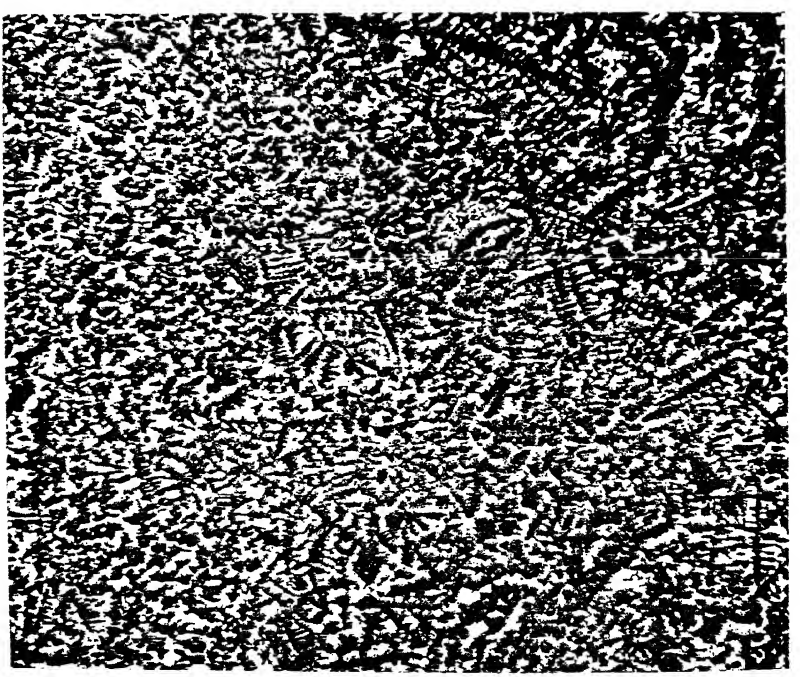


FIG. 195.



Macrostructure of a steel ingot.

Transverse sections from an 8-ton ingot of nickel-chromium steel.

FIG. 195.—Outside.

FIG. 196.—Half-way between centre and outside.
Etched with acid copper ammonium chloride solution. × 5.

On account of the chilling action of the mould, small crystals known as chill crystals, are formed at the edge of the ingot. These are succeeded by columnar crystals which have grown at right angles to the ingot surface. Since the rate of their growth is quickest in the direction of the steepest temperature gradient, no crystal orientated in a different direction has any chance of survival. Within the ingot where the temperature gradient is small, dendrites show a more irregular orientation. Here also crystallisation may start simultaneously from many different nucle and equiaxial grains are produced.

ultimately, they, as well as the equiaxial crystals, are broken down and their outer sheath of less pure material is extended into fibres in the direction of the increase in length produced by the forging or rolling. This gives the macrostructure the appearance of a material having a " grain " like that of wood. The properties of the region of equiaxial crystals as

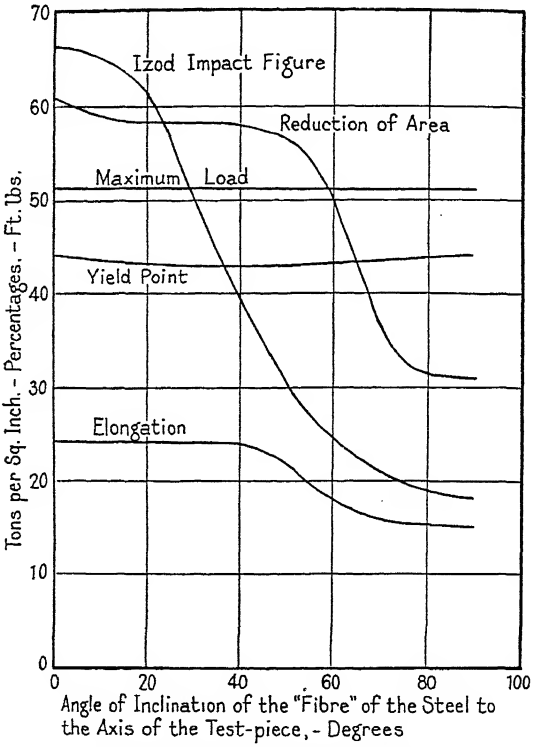


FIG. 197.—Relation between Mechanical Properties and Direction of Test-piece in Forged Steel. (*Brearley*.)

cast, and after heat treatment, are the same in all directions, but after the steel has been forged its properties depend very much on the direction with respect to " grain " in which it is tested. This is shown in Fig. 197, which illustrates the relationship between the mechanical properties of the steel and the angle of inclination of the fibres of the steel to the axis of the test-piece.

For this reason, in the macrostructure of any component of

an engineering structure the fibres or grain of the steel should always be at right angles to the principal shear or bending stress and should be parallel to the tensile stress. A glance at the macrostructure of such a component will reveal something of its history during manufacture, whether it has been forged to its finished form, or whether it has been machined, and if so at what positions: it will detect the presence of welds, their soundness and their effect on the surrounding metal: it will disclose lack of uniformity of composition, segregation and local defects, and in the examination of a component which has failed in service it may assist in the selection of regions for chemical analysis, mechanical tests or further microscopical examination.

Non-metallic Inclusions.—Before it is deoxidised, liquid steel always contains iron oxide and sulphide, either in solution or in suspension. The addition of ferromanganese for deoxidising results in the formation of manganese sulphide (probably containing iron sulphide in solution) and manganese oxide, which, reacting with the refractory lining of the ladle or combining with the silicon present in the steel, forms manganese silicate. These impurities exist in larger or smaller masses in suspension in the steel, and tend to rise to the surface. The rate of rise is, however, very slow for the smaller particles and many become trapped in the steel as it solidifies. The impurities manganese sulphide and silicate are probably those most commonly occurring in steel.

Manganese Sulphide (MnS) occurs in streaks or globules of a dove-grey colour (Fig. 205). It is elongated during rolling, and its form is unaltered by subsequent heat treatment. Hence the direction of the manganese sulphide inclusions reveals information regarding direction of forging or rolling even after complete recrystallisation of the metal has taken place (Fig. 202).

Iron Sulphide (FeS) occurs rarely in steels and is only present when there is insufficient manganese to ensure that all the sulphur occurs as manganese sulphide.

Macrostructures of alloy steel forgings.

FIG. 198.—Part of the transverse section of a forging about 17 inches square, forged from an octagonal ingot 26 inches across the flats. Coarse columnar crystals in the outer portion of the forging changing to equiaxial crystals in the central portion. Flaws in the form of hair-line cracks are visible on the left of the photograph. The dark etching line in the centre of the lower edge is not a crack but a line of high carbon content, originally a corner segregate in the ingot. The steel to right and left of this position came from adjacent sides of the octagonal ingot.

Etched with nitric acid in alcohol. Actual size.

FIG. 199.—Interdendritic segregation persisting after forging and heat treatment. The forging was similar to that from which Fig. 198 was taken, and had been annealed, oil-hardened and tempered. Diamond hardness tests (the impressions being visible in the photograph) showed differences as great as 36 in hardness between closely adjacent regions, the high-carbon dark-etching material being invariably harder than the purer light-etching material.

	Brinell hardness number.
Broad dark lines . .	270 and over
,, light regions . .	252 and under

The existence of such a degree of heterogeneity increases the risk of cracking during cooling after forging or during heat treatment, and indicates that the original dendritic segregation of the ingot must have been excessive.

Etched with ammonium persulphate solution. × 2·5

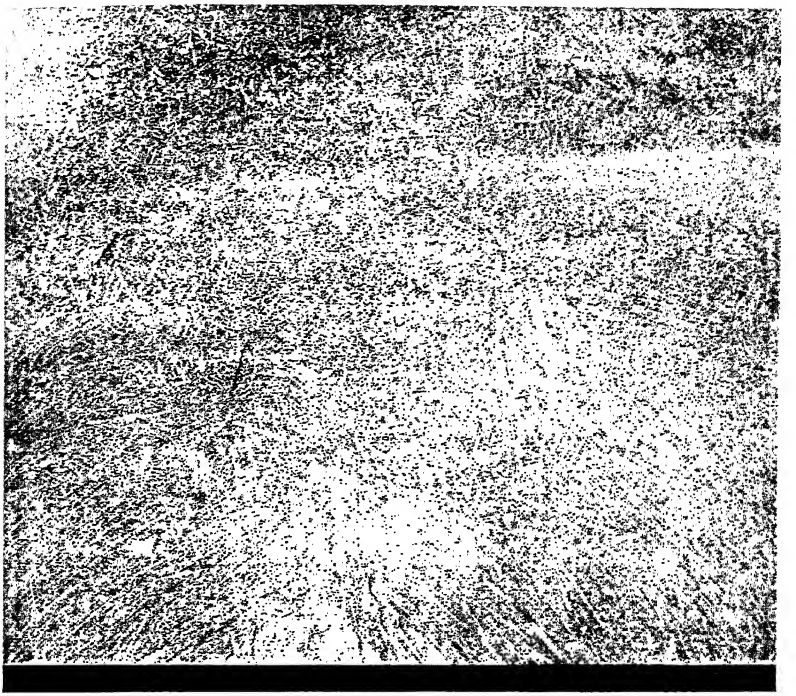


FIG. 198.

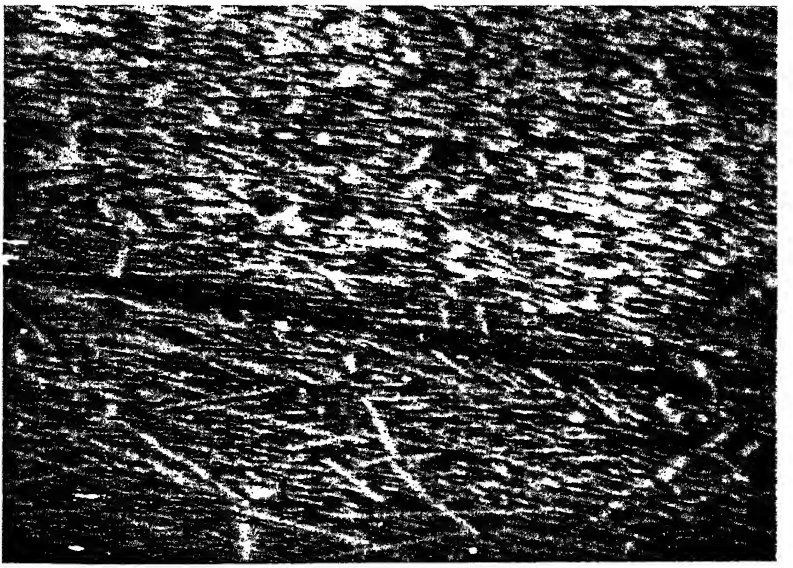


FIG. 199.

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PLATE XXXVIII.

FIG. 200.

FIG. 201.

FIG. 202.

FIG. 203.

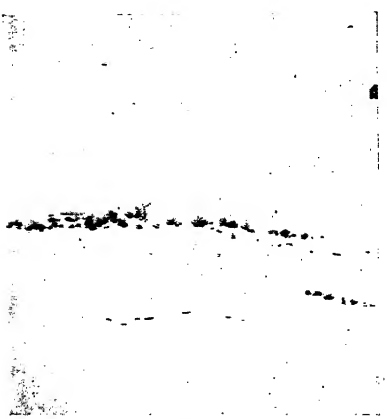

FIG. 204.

FIG. 205.

FIG. 200.—Interdendritic segregation of carbide in the steel of which the macrostructure is shown in Fig. 198. Air-hardened and tempered. Tensile test-pieces taken with their axes across these lines of segregation failed prematurely with very little elongation after the yield point was exceeded.

Etched with nitric acid in alcohol. × 50.

FIG. 201.—Transverse section across the bottom of a pipe showing slag inclusion.

Unetched. × 100.

FIG. 202.—Inclusion of manganese sulphide in a forging of 0·35 per cent. carbon steel, oil-hardened and tempered. The general structure consists of a ferrite network enclosing grains of coarse sorbite: the separation of ferrite round inclusions (as here shown) is commonly observed.

Etched with 1 per cent. nitric acid in alcohol. × 250.

FIG. 203.—Sulphide films (iron and manganese sulphides) in ferrite in a steel casting containing 0·4 per cent. carbon.

Etched with 1 per cent. nitric acid in alcohol. × 100.

FIG. 204.—Alumina in steel. Longitudinal section.

Unetched. × 100.

Fine particles, not elongated by hot-working but having the appearance of black specks; difficult to polish without scoring the surface.

FIG. 205.—Manganese sulphide in steel. Longitudinal section.

Unetched. × 100.

Dove-grey. Not affected by ordinary etching in alcoholic nitric acid, but blackened by etching five minutes in boiling alkaline sodium picrate.

It is of a brownish-yellow colour and sometimes occurs round the grain boundaries of cast steel. It is very infusible and does not ball up like manganese sulphide; hence it is injurious to the properties of steel and makes it red and cold short (*i.e.* brittle when worked hot or cold). The sulphide films shown in Fig. 203 have a duplex structure and probably contain a large proportion of iron sulphide.

Manganese Silicate is darker grey than the sulphide, but it is not always possible to distinguish between them with certainty under the microscope unless, as is often the case, they occur side by side. The distribution and amount of sulphide may, however, be revealed by "sulphur printing" and the appearance of the sulphur print compared with that of the section examined.

Slag Inclusions.—Dark-grey streaks in rolled material when present in large amounts usually represent inclusions of slag. They frequently show more than one constituent. Such inclusions are characteristic of wrought iron, but are rare in steel. When present there is frequently decarburisation in the neighbourhood of the slag. Fig. 201 shows slag spots from the region of the "pipe" in a billet of medium carbon steel. Slag is generally associated with the presence of piping (see p. 173). The surrounding steel is often completely decarburised, and then shows a strong resemblance to the structure of wrought iron.

Alumina (Al_2O_3).—Inclusions of alumina may occur in steels which have been "killed" by the addition of aluminium, alumina being formed by the reaction of iron oxide and aluminium. The alumina is hard and infusible. It is not deformed by work applied to the steel, though a group of particles of alumina may be drawn out into a streak, each member of the group remaining undeformed.

Alumina appears to drop out of the steel during polishing, the appearance of the microstructure being a collection of round black spots (Fig. 204). Small scratches originating at the boundaries of these specks are usually very difficult

to remove. They may be caused by alumina falling out during polishing, and scratching the surface.

Influence of Non-metallic Inclusions on the Properties of Steel.—Non-metallic inclusions have but little effect on the properties in the longitudinal direction, but if the steel is submitted to stress transversely, they form planes of weakness the effect of which is not measured simply by the area they occupy, since high localised stresses may be induced at the borders of the inclusions. Thus even with large amounts of inclusions the results of longitudinal tests in ductile materials are only slightly affected, while elongation in the transverse tensile test is very greatly reduced and failure occurs frequently in transverse bending tests. Non-metallic inclusions are an important factor in the heterogeneity which is responsible for the effect of direction of "grain" on mechanical properties, illustrated in Fig. 197. They may be associated with cracking in steel (Figs. 218 and 219) but are seldom the major cause of the trouble. Inclusions which by chance occur in a highly stressed region, for example, of an aircraft engine part, may have a serious effect in reducing endurance. Methods have been described of making inclusion counts. They all depend on microscopical examination and comparison with standard charts, and may be of value in investigations for producing cleaner steel, but difficulties of standardising sampling and in the interpretation of results make them unsuitable for general purposes.*

Manganese sulphide is the least harmful of the commonly occurring inclusions. Mild steel rod of high sulphur content may contain innumerable streaks of manganese sulphide, which do not seriously interfere with its strength, while they greatly facilitate machining. "Free cutting" mild steel usually contains about 0·1 per cent. of phosphorus in addition to 0·12 per cent. of sulphur. The high phosphorus content

* *Eighth Report on the Heterogeneity of Steel Ingots.* Iron and Steel Institute, Special Report No. 25.

FIG. 206.—Roke in steel bar, carbon 0·4 per cent. (ferrite and pearlite), showing decarburised area (absence of pearlite) round roke.

Etched with 5 per cent. nitric acid in alcohol. × 50.

FIG. 207.—Roke in steel bar, carbon 0·4 per cent., etched with Stead's reagent, showing the distribution of phosphorus and the irregularity of flow of the metal round the roke. The dark etching bands are those on which copper was deposited, and indicate the regions in which the phosphorus is lowest. × 25.

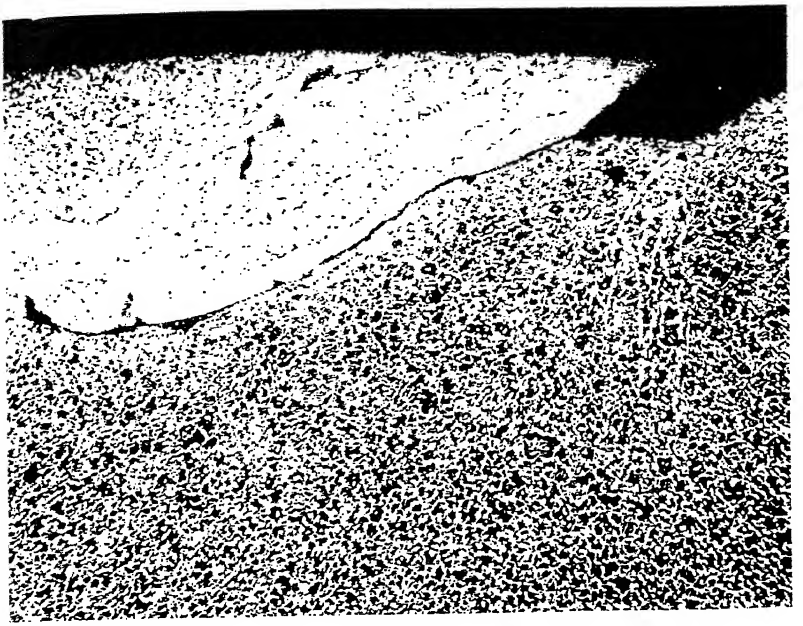

FIG. 206.

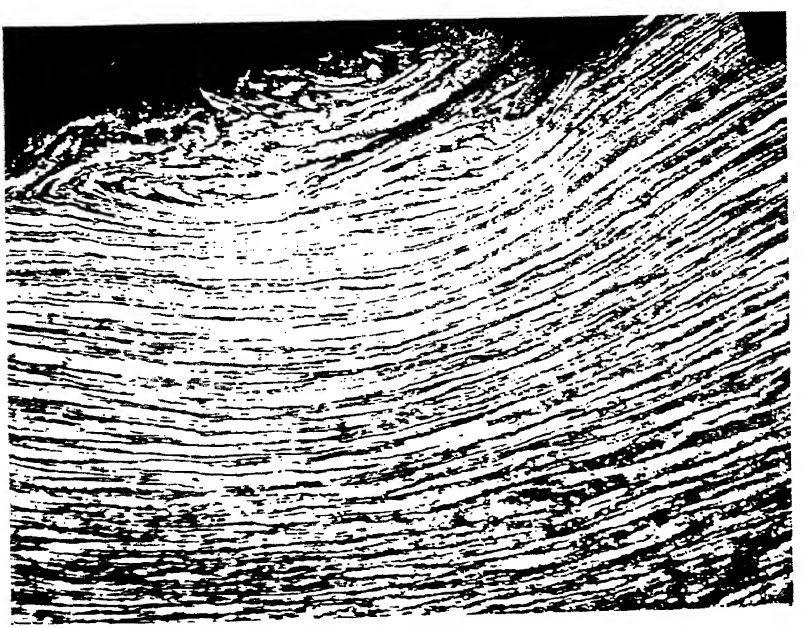

FIG. 207.

PLATE XL.

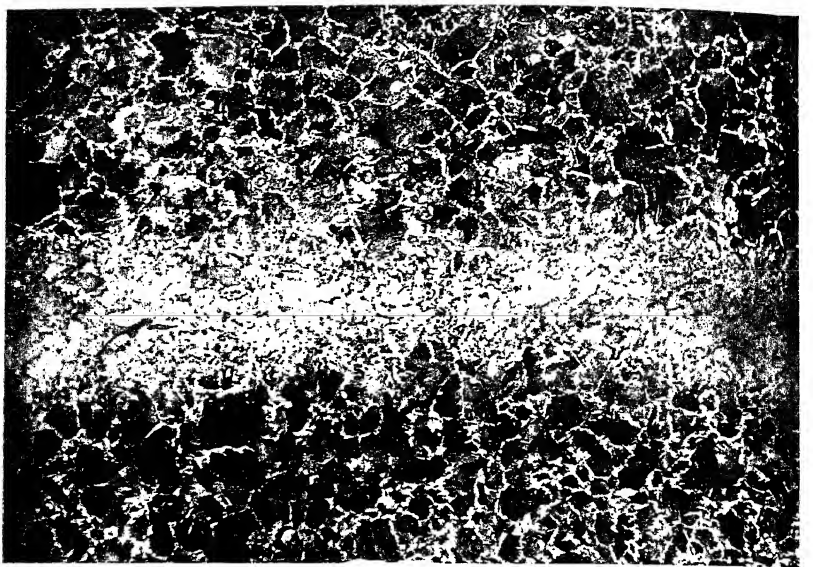

FIG. 208.

FIG. 209.

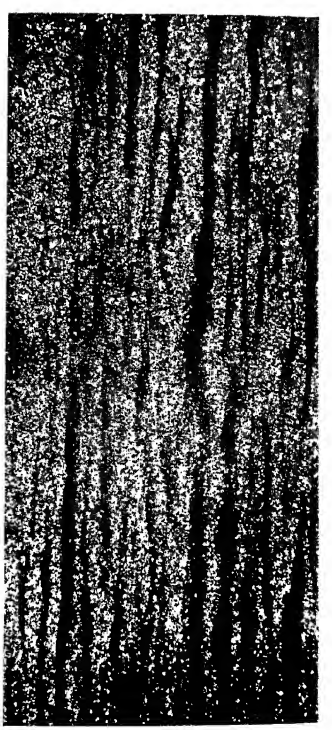

FIG. 210.

FIG. 208.—Ghost, consisting of ferrite rich in phosphorus, and containing inclusions of manganese sulphide in a heat-treated 0·45 per cent. carbon steel forging (ferrite network enclosing grains of sorbite). Longitudinal section. Etched with 2 per cent. nitric acid in alcohol.

× 100.

FIG. 209.—Transverse section from a nickel–chromium steel forging, showing dendritic structure. Etched with Stead's reagent. Oblique illumination.

The regions on which copper was not deposited are richest in phosphorus, and appear dark under oblique illumination. × 5.

FIG. 210.—Longitudinal section from the same forging. Etched with Stead's reagent. Oblique illumination. The dark streaks are ghost lines, rich in phosphorus.

× 5.

promotes the formation of chips instead of long spiral turnings, but it has an embrittling effect, which (especially in view of its liability to segregation) may be serious if the steel is used for highly stressed parts, such as bolts. As an alternative a low-phosphorus, high-sulphur steel can be used in a slightly cold-worked condition. The addition of 0·25 per cent. of lead to steel improves machineability. Though some of the lead collects in sulphide inclusions the effect appears to be due to a dispersion of lead not visible under the microscope.

Phosphorus Segregation.—Even in extreme cases of segregation, phosphorus in steel rarely reaches a concentration sufficient to cause the separation of a special constituent (as in Fig. 213), but an uneven distribution of phosphorus is no exceptional occurrence. There is an uneven distribution in the solid solution formed from a molten mass of mild steel, the cores of the crystals containing less phosphorus than the outside. Since diffusion of phosphorus is slow while carbon is readily expelled from areas rich in phosphorus, this segregation persists and finally the rolled or forged steel shows alternate bands of ferrite rich in phosphorus and of pearlite.

The distribution of phosphorus may be studied by etching with reagents containing cupric chloride, by the action of which a thin film of copper is deposited first on the regions containing least phosphorus (Figs. 209, 210). The phosphorus banding (*i.e.* the undeposited region rich in phosphorus) in a mild steel will frequently be found to cut across the ferrite grains, including one part and excluding another part of the same crystal.

Heat tinting shows a similar banding. Its persistence after deformation (even when subsequent heat treatment has been applied) frequently gives valuable information as to the direction in which flow has taken place under the mechanical treatment applied to the steel.

While phosphorus banding in a mild steel is not in any way abnormal, it may attain such proportions as to rank as

a defect, *e.g.* a high-phosphorus core in a mild steel rod, and it is a definite indication of inferior quality in a higher carbon steel.

Rokes are discoloured longitudinal marks, usually of small depth, on the exterior of a bar. They are due to blow-hole cavities lying just below the surface of the ingot. During rolling or forging the cavities may be broken into and their surfaces oxidised, and at the same time the whole defect is elongated in the direction of rolling. Rokes therefore consist of fissures (often partially closed) with their surfaces separated by a thin film of scale or other impurity. They extend below the surface to various depths.

The microstructure of a roke is shown in Figs. 206 and 207. The fissure is filled with a large inclusion of iron oxide of a dark bluish-grey colour, and the surrounding steel is decarburised.

Seams show a similar microscopical appearance to rokes and are caused in rolling billets or bars by one portion of the metal folding over another. The oxidised surfaces of the seam may subsequently partially weld up, the oxides reacting and causing local decarburisation round the defect.

Ghosts are marks which when viewed at a suitable angle are just visible on freshly machined surfaces. If the surfaces are left to tarnish slightly the ghost appears as a streak, frequently of considerable breadth, differing in colour from the rest of the steel. A ghost is due to local segregation of impurities during the solidification of the ingot. The segregated regions become elongated into streaks or lines during the rolling or forging of the metal.

The microstructure shows long threads of manganese sulphide in streaks of ferrite usually high in phosphorus (Fig. 208).

Piping.—This defect originates during solidification of the steel in the ingot-mould owing to the fact that solidification starts from the walls and proceeds inwards, and that steel contracts on solidification. The result is the formation

of a central cavity or cavities which, according to the conditions employed in casting, may extend to various distances downward in the ingot. Piping always takes place to a certain extent except in a "wild" cast (*i.e.* one in which blow-holes are formed throughout the ingot). It is limited to as short a length of the ingot as possible, and the unsound portion of the billet produced by rolling the ingot is discarded. If insufficient discard is made, piping, which may have escaped notice, may be present after rolling in the form of a longitudinal fissure or region of unsoundness in the central portion of the billet.

It is revealed in the microstructure in the form of ragged holes and cracks, the adjacent steel being usually very rich in inclusions and abnormal in composition (Figs. 201 and 211). In particular the phosphorus content is often very high (Fig. 212) owing to segregation, and locally may in exceptional cases reach such a figure that the iron–iron phosphide eutectic is formed (Fig. 213).

Burning.—Whilst overheated steel can be restored by suitable heat treatment (pp. 114, 129) there is a stage of excessive overheating in which the steel becomes burnt and the normal properties are beyond recovery. This stage is reached if the steel is heated to the temperature of incipient fusion. The more fusible constituents of the steel melt, and coalescing into globules are squeezed into the crystal boundaries or intercrystalline joints (Fig. 214). At this temperature also liberation of gas may occur, and carbon monoxide may be formed by reaction of the carbon of the steel with the layer of scale on the surface. These gases may not only form blisters, but may open up the surface skin for the expulsion of fluid material and the subsequent oxidation of intercrystalline cavities (Fig. 215).

A burnt steel is oxidised near the surface, but not necessarily throughout its mass, and even in the absence of an oxidising atmosphere the characteristic effects of "burning" may be produced.

Practical Notes

Surface Examination.—Deep etching with a 5 per cent. aqueous or 10 per cent. alcoholic solution of nitric acid is useful for revealing welds, local hardening, or minute cracks. The surface of the steel, after etching, is washed with acetone and dried: the acid, subsequently oozing up, stains the surface round the cracks and reveals them distinctly.

The presence of cracks may also be detected by a magnetic method. The sample is magnetised and (1) finely divided iron is blown on to its surface or (2) the surface is flooded with paraffin or similar liquid containing very fine iron dust in suspension. The particles of iron dust collect along the cracks, and are not displaced from this position when the rest of the surface is freed from iron (1) by an air blast or (2) by washing with clean paraffin.

Macrostructure

Examination of Sections.—The degree of finish required will depend on the fineness of the structure to be examined and on the etching agent employed. In most cases it is desirable to have the surface ground, though polishing is usually unnecessary. Absolute freedom of the surface from grease is essential if the etching is to be successful. If oil or grease gets on to the ground surface it is extremely difficult to remove, and a final cleaning with emery paper is preferable to the use of any degreasing reagent.

The preliminary examination should include sulphur printing and macro-etching.

Sulphur Printing.—A ground section perfectly clean and free from grease is obtained. Gaslight or bromide photographic paper is well soaked in 3 per cent. solution of sulphuric acid, placed face downwards on blotting-paper and lightly smoothed out with a squeegee to remove excess acid. It is then laid face downwards on the specimen, one edge being first applied and the opposite edge lowered until the surface is

covered. It is immediately rolled with the squeegee to obtain and preserve close contact, care being taken not to move the paper. A corner may be lifted to observe the progress of the printing, and after about 2 minutes the paper is held by the corner and peeled off the specimen. The print shows a brown coloration at positions where the paper has been in contact with sulphide. It is given a quick rinse in water to remove excess acid, then fixed in "hypo" and washed in the usual way, after which it is permanent. A second (paler) print may be obtained from the same surface, but it is better to have the section reground.

Macro-etching.—Reagents which act quickly for a short time generally give better results than slow reagents acting for a longer time. The principal reagents are nitric acid, copper ammonium chloride solutions and ammonium persulphate. The specimen, clean and free from grease, is usually placed in a trough and the appropriate reagent poured over the surface and renewed uniformly from time to time.

Nitric Acid.—If the specimen shows many grinding or machine marks a nitric acid etch is preferred. It is desirable to begin with 2 per cent. nitric acid, followed by acid of greater strength (5 to 8 per cent.), and to finish with 10 per cent. acid. In this way, scratches are eliminated and a fairly deep etch is obtained. Sulphur prints may be obtained from etched macro-sections. Such prints do not actually indicate the degree of sulphide segregation, but they record the macrostructure of the steel. The method may usefully be employed on alloy steels of high alloy and low sulphur content, from which neither a sulphur nor an ink print of the etched surface is readily obtainable in the usual way.

Copper Ammonium Chloride Solutions.—The most generally employed reagents for macro-etching are those which may be classed together as the cupric reagents. The 8 per cent. copper ammonium chloride solution, originally recommended by Heyn, has been modified by later investigators to adapt it on the one hand to deeper and sharper

etching of macrostructures, and on the other to more delicate etching of sections to be examined at higher magnifications. For macro-etching, a fairly good surface is required: if many deep scratches or machine marks are visible a preliminary etch with nitric acid is desirable. In Humfrey's modification of Heyn's method, a solution of 120 grams of cupric ammonium chloride in 1 litre of water is poured at frequent intervals over the roughly polished surface of the specimen so that a film of fresh solution is always in action. As etching proceeds, a similar solution acidified by the addition of 20 to 50 c.c. of hydrochloric acid per litre may be used. The copper deposit from an acid solution would adhere to the steel: the initial treatment with neutral solution provides an underlying loosely adherent layer, facilitating removal of the copper. When the copper deposit has been wiped away and the specimen washed and dried, the surface has a grey matte appearance. If it is lightly rubbed over with fine emery paper the portions in relief are brought out in sharp contrast. The time taken for the etching is ½ to 1 hour. To produce stronger relief effects in heavy ingot sections, which cannot be so well prepared as small specimens, the Iron and Steel Institute Committee on the Heterogeneity of Steel Ingots recommends etching for an additional half-hour with solution containing 15 per cent. of hydrochloric acid, possibly with an intermediate period in which a solution containing 7½ to 10 per cent. is used and a subsequent period in which still stronger acid solutions are employed if necessary.

Permanent records of the structure (macro-prints) may be obtained by Humfrey's method. For this purpose the macro-section should be machined to a flat slab, one of its parallel faces being selected for etching. When a satisfactory etch has been obtained, ordinary printer's ink is applied to the surface by means of a roller, *e.g.* a squeegee. A few dabs of printer's ink are placed on a sheet of glass or of tin plate and the roller is passed in all directions over the sheet until the ink is evenly spread out. Ink is transferred to the specimen by

passing the roller alternately over the inked plate and the etched surface. The specimen is then placed face upwards on the base of an ordinary copying press, the paper laid on it, covered with a pad and pressure applied. The best results are usually obtained on glossy art paper. The portions in relief, and thus the dark areas in the prints, represent the less pure material. The results on basic steels are apt to be disappointing.

Ammonium Persulphate.—The action of ammonium persulphate is much more superficial than that of the other macro-etching reagents described above. For this reason as good a finish as possible is required on the specimen to be etched, and the result can only be recorded by photography and not by macro-prints.

A 10 per cent. solution of ammonium persulphate in water is most suitable, though a stronger solution may be used. The specimen should be wholly immersed in the freshly prepared solution. As etching proceeds the immersed surface may be rubbed with a swab of cotton-wool, and on its completion the specimen is washed in water and dried, without rubbing, in the usual way.

Ammonium persulphate etching gives very clear indications of heterogeneity; it is a clean reagent to use, having much less action on the skin than acids or copper solutions, and its action is rapid, the time required for macro-etching varying from 5 to 30 minutes. In addition, differences in heat treatment, for example in degree of tempering, are indicated by variations in surface appearance.

Pickling in Sulphuric Acid.—A severe test for revealing heterogeneity consists in immersion of the specimen in 20 per cent. sulphuric acid at 80° C. This must be carried out in a fume cupboard or in the case of large specimens in the open air, the acid being contained in a suitable sheet-lead trough heated by ring burners.

The less pure parts and regions of unsoundness are rapidly attacked. After about 10 to 30 minutes the specimen is

removed from the acid, thoroughly washed with water, scrubbed with a brush in running water to remove the carbonaceous deposit and dried after washing with alcohol or acetone.

Deep Etching of Alloy Steel Ingot Sections.—A strong macro-etching is required to reveal unsoundness and porosity; the milder etching which serves to indicate the macrostructure sometimes gives no indication of porosity existing down the centre or elsewhere, together with the beginning of the unsoundness which develops into the pipe nearer the top. Some alloy steels can only be macro-etched to the required extent with difficulty. The following method may be tried in extreme cases. The ingot is mounted on trestles in the open air, on a day when there is just a slight breeze. The surface is levelled carefully, and a small fireclay wall built round its edge, of sufficient height to retain a layer of liquid at least $\frac{1}{4}$ inch deep on the surface. Gas burners are used to warm up the metal and to dry the fireclay. The heating is then withdrawn and a mixture of about one part of strong nitric acid to two parts of hot water applied. Care should be taken to keep away from the copious nitric oxide fumes evolved. When the action has subsided a small fragment of the fireclay wall may be removed and the spent liquid allowed to drain away and, if necessary, the wall made good and the action repeated.

Microstructure

Micro-etching.—From visual appearance and macro-examination, the regions which appear most likely to yield interesting results can be selected for ordinary microscopical examination. A small specimen of the usual type is prepared and examined: (1) unetched, (2) etched with 2 per cent. nitric acid in alcohol, and (3) copper etched to reveal the distribution of phosphorus.

The principal cupric chloride reagents for the detection of minor segregation in steel are:—

(*a*) Stead's reagent.

Cupric chloride	10 grams.
Magnesium chloride	40 grams.
Concentrated hydrochloric acid	20 c.c.

The salts are dissolved in the least possible quantity of water and the solution is made up to 1000 c.c. with alcohol.

(*b*) The N.P.L. reagent (Rosenhain and Haughton).

Ferric chloride	30 grams.
Cupric chloride	1·0 gram.
Stannous chloride	0·5 gram.
Concentrated hydrochloric acid	100 c.c.
Water	1000 c.c.

In carrying out copper etching a few drops of the reagent are poured on the specimen until it is covered with a thin layer of liquid. It is allowed to stand for 1 minute. The reagent is then shaken off and a fresh layer applied, the process being repeated as often as is found desirable. The specimen is then washed with hot water and dried in acetone. Copper is deposited on the regions in which the phosphorus content is lowest.

The exact identification of non-metallic inclusions in steel is a difficult problem,* and some of the methods of examination recommended (such as reduction in hydrogen) require the construction of special apparatus and involve considerable experimental difficulties. An approximate identification can be made as follows:—

(*a*) By appearance.

Iron sulphide	Brownish-yellow.
Manganese sulphide	Dove-grey.
Oxide of iron or manganese	Similar but darker.
Silicate of manganese	Dark slate-grey.
Silicate of iron	Nearly black.
Alumina	Round specks, never elongated.

* For a detailed study of the subject, see C. Benedicks and H. Löfquist, "Non-metallic Inclusions in Iron and Steel."

(*b*) By comparing a sulphur print of the unetched micro-section with its appearance under the microscope. Inclusions not revealed in the print are not sulphides.

(*c*) By etching with a 2 per cent. solution of hydrofluoric acid in alcohol for a few seconds. Sulphides and silicates are blackened but oxides remain unchanged.

CHAPTER XI

THE STRUCTURE AND PROPERTIES OF PIG IRON, CAST IRON AND MALLEABLE CAST IRON

Pig Iron—the product of the blast furnace—is the most impure form of commercial iron. The effect of various elements occurring in pig iron is briefly summarised below.

Carbon varies from about 2 to 4 per cent., and is generally about 3·5 per cent. Part is chemically combined with the iron forming Fe_3C: the rest occurs in the form of black flakes of graphite. The amount of combined carbon present has a great influence on the properties of the iron; as in the case of steels, increase of combined carbon gives increased hardness and up to a certain point increased strength. Thus 0·7 per cent. of combined carbon gives maximum tensile strength and 1·0 per cent. gives maximum crushing strength.

Good figures for these maxima would be 18 tons per sq. in. in tension and 70 tons per sq. in. in compression respectively. An extremely weak cast iron might give 5 tons per sq. in. in tension or 20 tons per sq. in. in compression.

The graphite has a weakening influence, most marked when it occurs in large flakes. Since the total carbon in commercial irons does not vary greatly, reduction of the amount of combined carbon is accompanied by increase in amount of graphite, and *vice versa*. Thus soft irons as a rule contain a large amount of graphite and break with a grey fracture, showing plates of graphite, while the hardest irons break with a white fracture and show little or no graphite.

This difference is the basis of the method of grading pig iron by fracture into grey, mottled and white iron, and of further sub-dividing grey iron for example, into No. 1,

No. 2, No. 3, No. 4 foundry, No. 4 forge, or some other numerical classification.

There are great variations of composition between the pig irons produced from different ores, but in any particular make of pig iron the increase of combined carbon and decrease of graphite passing from grey to white are accompanied by a slight fall in the total carbon, while silicon diminishes from grey to white, manganese diminishes slightly from grey to white, phosphorus remains constant, and sulphur increases from grey to white.

Silicon is always present in amounts usually varying from 1 to 3·5 per cent. It has a controlling influence on the properties of the iron; high silicon favours the separation of graphite, while in low-silicon irons more of the carbon is in the combined state.

For ordinary rates of cooling a pig iron with 3·5 per cent. of carbon will be white when the silicon does not exceed 0·6 per cent. The greatest crushing strength is produced by 0·8 to 1·0 per cent. of silicon, the greatest tensile strength with about 1·8 per cent. of silicon, while 2·5 per cent. will produce a soft iron.

Manganese occurs in part as carbide, Mn_3C, which resists decomposition by silicon better than Fe_3C. Manganese therefore tends to increase the amount of combined carbon, and so has a hardening influence on the iron. Some of the manganese occurs in combination with sulphur, and some may be in solid solution in the iron (ferrite).

Sulphur occurs as manganese sulphide if sufficient manganese is present, otherwise as iron sulphide. In the latter form it has the property of hardening the casting, but at the same time it makes it more brittle. The addition of manganese (itself a hardening element) to a hard high-sulphur cast iron results in softening, on account of the formation of the less harmful manganese sulphide and its partial elimination. Sulphur in any form is objectionable and should be as low as possible.

FIG. 211.—Section across the bottom of a pipe in 0·4 per cent carbon steel, showing cavities and sulphide inclusions
Unetched. × 100.

FIG. 212.—The same field as in Fig. 211, etched with Stead's reagent. The light areas on which no copper has been deposited are richest in phosphorus. × 100.

FIG. 213.—Iron–iron phosphide eutectic enclosed in pearlite occurring near the pipe in a 0·4 per cent. carbon steel
Etched with 1 per cent. nitric acid in alcohol.
× 1000.

FIG. 214.—Distribution of inclusions in the ferrite forming the boundaries of pearlite grains in a burnt steel.
Etched with 1 per cent. nitric acid in alcohol.
× 100.

FIG. 215.—Burnt steel, 0·7 per cent. carbon, showing large grain size, intercrystalline cracks and decarburisation.
Etched with 5 per cent. nitric acid in alcohol.
× 100.

FIG. 216.—Mild steel plate, carbon 0·08 per cent., showing intercrystalline cracks in the ferrite. These were produced by the action of a hot sodium nitrate solution, while the steel was subjected to a bending stress.
Etched with 5 per cent. nitric acid in alcohol.
× 100.

FIG. 211.

FIG. 212.

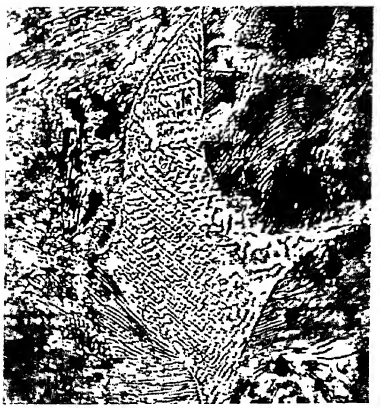

FIG. 213.

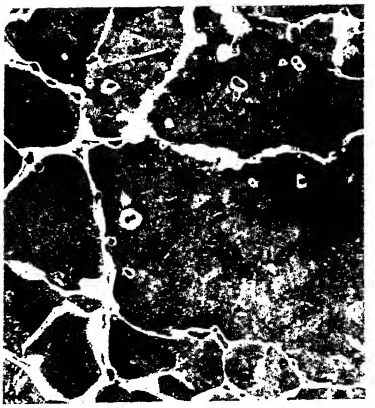

FIG. 214.

FIG. 215.

FIG. 216.

[*Facing p.* 184.

PLATE XLII.

FIG. 217.

FIG. 218.

FIG. 219.

Defects in steel.

Etched with nitric acid in alcohol.

FIG. 217.—Crack in micro-segregated region of an oil-hardened and tempered nickel–chromium–molybdenum steel of Brinell hardness 300. Diamond hardness tests showed differences of over 50 in hardness between closely adjacent regions. This indicates excessive inter-dendritic segregation in the original ingot. × 100.

FIGS. 218 and 219.—Cracks associated with non-metallic inclusions in the martensite of a hardened nickel–chromium steel. The cracks may have been formed during the cooling after forging or during the hardening process. They were not associated with micro-segregation of the type shown in Fig. 217.

Fig. 219 is a composite photograph (3 exposures) taken by blue light from a mercury lamp with a monochromat, N.A. 1·60.

Magnifications. Fig. 218, × 500.
Fig. 219, × 2500.

Phosphorus increases the fluidity of cast iron and lowers the melting point. Hence for making ingot moulds hæmatite irons low in phosphorus are used, while for ornamental castings of thin section in which fine details of the pattern are to be reproduced the phosphorus in the pig iron used may be as high as 2 per cent. For ordinary good strong casting pig iron with about 0·5 per cent. phosphorus is satisfactory.

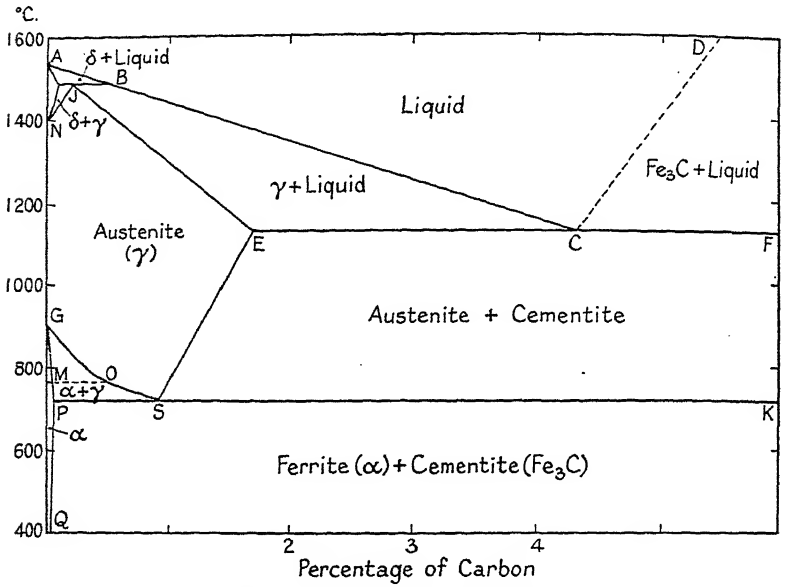

FIG. 220.—Iron–Carbon Diagram.

Cast Iron.—When pig iron is remelted and cast into its final form it is known as cast iron. Whereas pig iron is always cooled relatively slowly, castings may vary enormously in their rate of cooling. The microstructure and properties vary in a corresponding way. The faster the cooling the smaller and fewer will be the graphite particles. By the use of a mould part of which is of cast iron (as, for example, in the production of chilled rolls), rapid cooling is obtained and a metal, white at the surface, is produced. The behaviour is best indicated by reference to the constitutional diagram, but the warning given in the case of steel must be emphasised

in the case of the richer carbon alloys of iron. Both stable and unstable conditions have to be accounted for, and the practical interpretation of the diagram is always complicated by the presence of impurities in the iron. Fig. 220 shows the iron–carbon diagram and illustrates the constitution of white iron. Cast iron at the moment of solidification consists of solid solution (austenite) containing 1·7 per cent. of carbon and a eutectic of austenite and cementite containing 4·3 per cent. of carbon. As cooling proceeds, more cementite separates from the solid solution, until this contains 0·9 per cent. of carbon. At 690° C. all the remaining solid solution (containing 0·9 per cent. of carbon) breaks down into pearlite, giving finally the structure of cementite and pearlite typical of white iron (Figs. 223, 233).

It is probable that all liquid cast iron (whether white or grey in the cold state) first begins to solidify in a similar way to give solid solution and cementite–solid solution eutectic. The distinctions between white and grey iron are developed subsequently to complete solidification. The separation of graphite is due to the decomposition, during cooling, of cementite. This is accompanied by an evolution of heat and expansion in volume. The slower the rate of cooling the more graphite will be formed. The size of the graphite plates separated at the moment of solidification is large: graphite formed considerably below the melting point is smaller and more evenly distributed.

The presence of sulphur or manganese, as we have seen, hinders the separation of graphite; so also does chromium, so that irons rich in manganese or chromium are permanently white, and no rate of slow cooling will make them grey. On the other hand, the presence of silicon promotes the decomposition of carbide, and irons containing 3·5 per cent. of silicon are grey even when rapidly cooled in castings of small section. When phosphorus is present the temperature of final solidification is depressed to 943° C., and a liquid iron which contained 2 per cent. of carbon and 6·7 per cent. of phos-

phorus would solidify as a whole at this temperature to form a triple eutectic of iron–iron carbide–iron phosphide. This constituent is formed at the moment of solidification of any iron rich in phosphorus, but it is not preserved unchanged. As the separation of graphite proceeds, the carbide diffuses out of the eutectic, leaving only the binary eutectic of iron–iron phosphide containing 10·2 per cent. of phosphorus.

Microstructure of Pig Iron and Cast Iron.—In a previous chapter the change in the structure of steel has been considered with change of carbon content up to about 1·5 per cent. If the amount of combined carbon present is assumed to

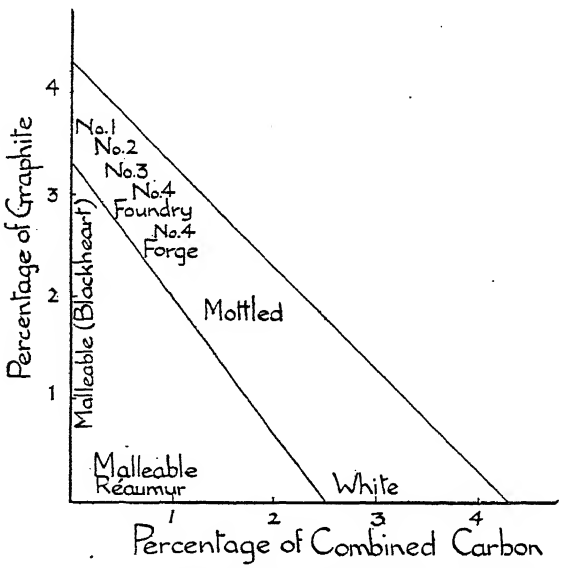

FIG. 221.—Diagram indicating the Condition of Carbon in Pig Irons, etc. (After *Howe*.)

increase without the formation of graphite, the composition of a very pure white iron is reached. The microstructure of such an iron (American washed iron) is shown in Fig. 223. Like a high-carbon steel, it consists only of pearlite and cementite.

The microstructure of pig irons is modified, and their mechanical properties are profoundly influenced, by the fact that part of the carbon they contain separates as graphite,

while part of it remains in the combined condition. To simplify the interpretation of the structures encountered in grey pig irons, it is most convenient to regard them in the light of impure steels of the composition corresponding to their content of combined carbon. Thus, referring to the diagram (Fig. 221) showing the relation between combined and graphitic carbon in different varieties of cast iron, the structure of No. 1 iron may be considered as graphite set in a groundmass of a very impure steel containing 0·2 per cent. of carbon. It is further necessary to consider the effect on the microstructure of the various impurities in turn, and to regard the graphite as an additional constituent whose characteristics can be studied separately.

The structure of hæmatite irons may therefore be regarded as graphite incorporated in the structure of a steel containing the same amount of combined carbon, but modified by the presence of a considerable amount of silicon and some manganese. For example, Figs. 224 and 225 show a No. 2 hæmatite pig iron, containing 3·5 per cent. graphite and 0·4 per cent. combined carbon. The structure shows ferrite and pearlite, the graphite occurring in large plates in the ferrite. The silicon is in solid solution in the ferrite as silicide of iron (silico-ferrite). Presence of high manganese tends to make the pearlite irresolvable. A No. 1 hæmatite iron is similar, but contains more ferrite. No. 4 hæmatite irons contain about 0·8 to 1·0 per cent. of combined carbon. These are almost completely pearlitic, some containing a little free cementite: the graphite is less in amount and as a rule finer in dimensions (Fig. 226).

Intermediate between No. 4 iron, containing a little cementite, and white iron there occurs mottled iron (Fig. 227), in which the structures of grey and white irons are juxtaposed —a feature which gives the characteristic mottled appearance to the fracture.

The process of solidification in phosphoric irons has already been considered. In grey irons containing phosphorus the

silico-ferrite forms round the graphite plates, forcing inwards the fusible iron–iron phosphide eutectic, which finally solidifies in positions remote from the graphite, assuming a characteristic herring-bone structure (Figs. 228, 229).

The phosphide eutectic is the last constituent attacked by deep etching with 1·2 sp. gr. nitric acid, and its distribution may be examined on the black background produced by this reagent (Fig. 230). With high phosphorus content there is a tendency to liquation, and hard shots of metal containing as much as 10 per cent. of phosphorus may exist in blow-hole cavities in the casting. Figs. 231 and 232 show the structure of one of these hard nodules.

In white irons containing phosphorus the eutectic always contains cementite in addition to iron–iron phosphide. This may be revealed by heat tinting, the phosphide remaining yellow after the other constituents are coloured.

Low-grade irons show, in addition to a large proportion of phosphide eutectic, films and blobs of iron and manganese sulphides. Ferrite when present is apt to show stains after etching, and pearlite is often irresolvable.

Malleable Cast Iron.—It will be recalled that the cementite of a high-carbon steel, on prolonged annealing at a high temperature, decomposes into graphite and ferrite. A precisely similar action takes place more readily when a white iron (containing cementite and pearlite) is heated in the American or Blackheart process of making malleable cast iron.

Fig. 233 shows a white iron consisting of pearlite and cementite: the structure after prolonged heating at 750–800° C. is shown in Fig. 234. Decomposition of the carbide has proceeded with the deposition of graphite in a very finely divided state in a groundmass of ferrite. Frequently a little pearlite remains without detriment to the properties of the casting (Fig. 235). It is the finely divided graphite, or "temper carbon," as it is called, which gives the fracture of the casting its black appearance and so gives the process its name.

A curious feature which frequently occurs in Blackheart castings is a ring of pearlite running through the ferrite parallel to and near the outer edge (Fig. 241). The probable explanation of this ring is that the ferrite outside is produced by decarburisation of the skin, while that inside is produced by deposition of graphite, leaving an intermediate layer in which the combined carbon, reduced by decarburisation, is insufficient to cause precipitation of graphite.

The packing material used is sand or preferably scale, the temperature of heating, 750° to 850° C., varying with composition. The time necessary to achieve the complete deposition of carbon varies from a few hours to several days, according to the thickness of the material and its composition. For the production of a Blackheart malleable casting the sulphur of the original white iron must be below 0·1 per cent.; phosphorus should be below 0·2 per cent., and manganese under 0·5 per cent. Malleable castings of this type have a tensile strength of 16 to 26 tons per sq. in. and give an elongation of 5 to 15 per cent.

Another form of treatment, at one time the only method used in Europe, known as the Réaumur process, consists of heating white iron castings at 850° to 900° C. in an oxidising medium such as hæmatite ore. A wider range of composition is permissible in the original white iron, which, however, should not contain more than 0·2 per cent. of phosphorus. The first effect of heating in this process also is the precipitation of temper carbon, but this is subsequently oxidised away, leaving a product which is mainly pearlitic (Fig. 236). Fig. 237 shows partial precipitation of graphite from massive cementite in the centre of a malleable casting. Direct decarburisation of the carbide without previous decomposition also occurs.

In microstructure, malleable cast iron produced by the Réaumur process resembles steel to some extent; though the structure is modified by the prolonged heating, the pearlite is invariably coarser, and traces of temper carbon frequently

remain (Fig. 238). On account of the decarburisation the structure varies from centre to outside. Figs. 237 to 240 form a series of photographs taken at intervals from centre to outside of a malleable casting. The centre shows appreciable amounts of temper carbon, while the outside shows little but ferrite. This ferrite is not, however, the pure ferrite of steel: the properties are also affected by the high sulphur content and possibly by penetration of oxide from the packing medium.

Such castings have a grey steely fracture. They show a tensile strength of 20 to 28 tons per sq. in. with an elongation of 3 to 6 per cent. They are capable of being bent or dressed by a hammer, but they are less ductile than Blackheart castings. There is, however, no sharp distinction between the two types: they merge into one another according to the treatment, the packing material employed and the composition of the original casting, particularly as regards sulphur content. Both types of malleable cast iron are liable to suffer from defects, such as blow-holes, present in the original white iron casting.

Alloy Cast Iron.—The properties of a cast iron depend mainly on the condition of the carbon, whether it exists as graphite or as carbide of iron, and if as carbide whether this constituent occurs in the massive form or as the eutectoid, pearlite. A completely pearlitic structure (Fig. 242) is for many purposes most desirable, as it combines machinability with resistance to wear. To secure such a structure under normal casting conditions involves the use of a low-silicon iron. The condition of the carbon is also dependent on the proportion of other elements present, in particular each of the possible alloying elements, aluminium, nickel, chromium, molybdenum and vanadium, has a characteristic effect. Thus nickel and aluminium act like silicon, reducing the tendency of the carbon to form carbide and increasing the amount of graphite; while chromium, molybdenum and vanadium increase the tendency to form carbide and facilitate the production of hard white iron.

The addition of 1·5 per cent. of nickel renders a 1 per cent. silicon white iron pearlitic in structure and readily machinable, while it has little effect on the condition of carbon in a high-silicon grey iron. Chromium, on the other hand, reduces the amount of graphite and increases the amount of carbide in grey iron, but leaves the condition of the carbon in white iron unaffected except to render the carbide more resistant to decomposition by annealing. The effect of the alloy elements is by no means confined to their influence on the condition of the carbon. In cast iron, as in the alloy steels, the added elements have a characteristic effect on the structure, and therefore on the properties, of the pearlite; and when present in large amounts they induce similar constitutional changes to those noted in the alloy steels.

Thus the usual lamellar pearlite is made finer and ultimately rendered sorbitic by the presence of alloy elements in small amounts. Larger amounts confer air-hardening properties. A nickel cast iron containing 5 per cent. of nickel is martensitic as cast, one with 20 per cent. of nickel or 10 per cent. of nickel and 5 per cent. of manganese is austenitic and non-magnetic (Figs. 243 and 244). Chromium confers the characteristic properties of resistance to wear, to corrosion and to oxidation at high temperatures.

Nickel and chromium are used together to refine the structure and increase the hardness and strength of cast iron without impairing its machinability. Nickel alone can only give the eutectoid composition if silicon is low, chromium alone if silicon is high. The proportions of the two may, however, be so adjusted that with the ordinary silicon content of about 2·5 per cent. they neutralise one another with respect to their influence on the condition of the carbon, but each contributes its own effect in modifying the structure of the pearlite and in increasing strength, toughness and resistance to wear. Such an effect is produced by a ratio of nickel to chromium of about $2\frac{1}{2}:1$; for example, by the addition of 1·3 per cent. of nickel and 0·5 per cent. of chromium.

All (except Fig. 224) etched with nitric acid. Magnification 100 diameters.

FIG. 222.—Hair-line crack in oil-hardened and tempered nickel-chromium steel.

FIG. 223.—American washed iron (combined carbon 3·5 per cent., graphite nil) showing cementite (white) and pearlite (dark).

FIG. 224.—No. 2 hæmatite pig iron (combined carbon 0·4 per cent., graphite 3·5 per cent.).
Unetched, showing flakes of graphite.

FIG. 225.—The same pig iron as in Fig. 224, etched, showing graphite (black), ferrite (white, near graphite) and pearlite.

FIG. 226.—No. 4 hæmatite pig iron, showing graphite (black), cementite (white, remote from graphite) and pearlite.

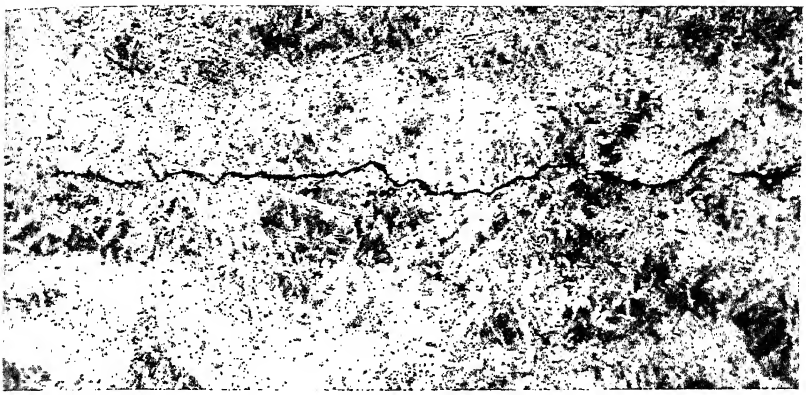

FIG. 222.

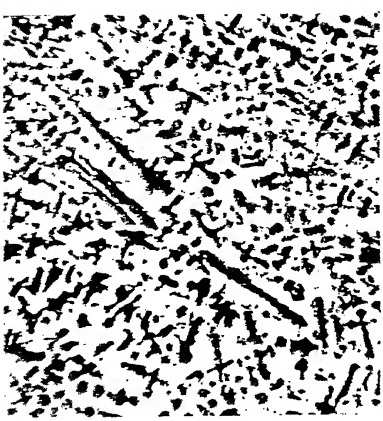

FIG. 223.

FIG. 224.

FIG. 225.

FIG. 226.

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FIG. 227.

FIG. 228.

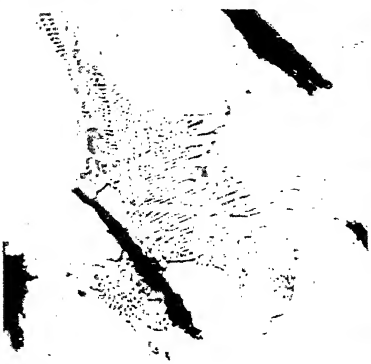

FIG. 229.

FIG. 230.

FIG. 231.

FIG. 232.

All (except Fig. 230) etched with nitric acid in alcohol.

FIG. 227.—Mottled iron, showing the structures of white iron (cementite and pearlite) above, and grey iron (graphite and pearlite) below. × 100.

FIG. 228.—No. 2 Northampton pig iron (phosphorus 1·1 per cent.) showing graphite (black), ferrite (white, near graphite), pearlite (half-tone) and phosphide eutectic (remote from graphite). × 100.

FIG. 229.—Structure of the iron–iron phosphide eutectic in phosphoric pig iron. × 500.

FIG. 230.—No. 2 Northampton pig iron (Fig. 228), deeply etched with 1·2 sp. gr. nitric acid. The phosphide areas are unattacked. × 100.

FIG. 231.—Structure of a phosphoric nodule (containing 8 per cent. of phosphorus) in cast iron. Ferrite containing about 1·7 per cent. of phosphorus (dark) and iron phosphide Fe_3P (white). × 50.

FIG. 232.—The same as Fig. 231. × 500.

Alloy cast irons often benefit by heat treatment. The matrix of a nickel–chromium cast iron of the composition given above is sorbitic pearlite, the laminæ of which are barely resolvable at 1000 diameters. On heat treatment, this goes through the usual structural changes; when oil-hardened from 850° C. it becomes martensitic, tempering at 500° C. converts this into sorbite, the particles of which increase in size with increasing tempering temperature, giving a structure consisting of coalesced carbide in a ferrite groundmass after reheating at 650° to 700° C.

Practical Notes

Polishing of white cast iron presents no difficulty, but grey cast iron, the constituents of which differ widely in hardness, requires greater care unless a structure showing visible pits from which the graphite has been torn out can be accepted. For many purposes such structures give all the information that is desired; but sometimes, especially when the form and structure of the graphite is being investigated, the graphite itself must be polished and all precautions, indicated on page 9, taken to avoid either the opening up or closing over of the cavities containing this soft and friable material.

The structure should in the first instance always be examined before etching to note the size, distribution, and amount of graphite. Regions rich in phosphorus and carbide often appear in relief after polishing. For special examination of the graphite the preliminary polishing may be followed by alternate prolonged etching in 5 per cent. alcoholic nitric acid, and polishing with diamantine.

Etching.—For most cast irons containing pearlite a 2 per cent. solution of nitric acid in alcohol, or a 5 per cent. solution of picric acid in alcohol.

For those with little pearlite, and for Blackheart malleable cast iron a 5 per cent. solution of nitric acid in alcohol or a saturated solution of picric acid in alcohol.

Wash with alcohol or acetone. Persistent staining round

graphite particles may often be avoided by prolonged soaking in acetone before drying or by a final wash with ether, after which drying occurs very rapidly.*

An alkaline solution of sodium picrate darkens cementite in cast iron in the same way as in steel (p. 120); it also darkens iron phosphide, Fe_3P, and cannot, therefore, be used to distinguish between the two, but a neutral sodium picrate solution (Matweieff's reagent) used boiling, attacks Fe_3P in 20 minutes leaving cementite unaffected. The distribution of phosphorus in solid solution in the iron may be revealed by etching with copper reagents (p. 180). Very deep etching with 1·2 sp. gr. nitric acid leaves highly phosphoric regions bright.

Heat tinting is carried out as described on page 18. It is advisable to give the specimen a light etch with 2 per cent. alcoholic nitric acid solution before heat tinting. The sequence of heat tints obtained with a steadily rising temperature of 200° to 400° C., is as follows:—

Pearlite, 0·75% C., 0·6% P.	Ferrite. 1·7% P.	Cementite, Fe_3C.	Phosphide, Fe_3P.	Manganese Sulphide.
Yellow.	Pale yellow.	White.	White.	Dove-grey.
Brown.	Yellow-brown.	Pale yellow.	,,	,,
Red-purple.	Brown.	Yellow.	V. pale yellow.	Pale yellow.
Purple.	Red-purple.	Yellow-brown.	,, ,,	,, ,,
Blue.	Purple.	Brown.	Pale yellow.	Pale yellow.
Pale blue.	Pale blue.	Red-brown.	Heliotrope.	Brownish-white.
Pale pea-green.	,, ,,	Purple.	Greenish-yellow.	Brownish-white.

A general blue-purple appearance, corresponding to the tints interlined, should be aimed at. A similar sequence of colours is produced by holding the specimen at a temperature of about 300° C., cementite becoming reddish-brown and phosphide remaining pale yellow after about 10 minutes' heating.

* For special examination of the structure of graphite and other inclusions, see H. Morrogh, "The Metallography of Inclusions in Cast Irons and Pig Irons," *Journal of the Iron and Steel Institute*, 1941, No. 1.

All etched with nitric acid in alcohol.

FIG. 233.—White cast iron, as used in the manufacture of malleable cast iron. Pearlite (dark) and cementite (white). × 100.

FIG. 234.—Blackheart malleable cast iron. The same white iron as in Fig. 233 after annealing, showing graphite (black) in a groundmass of ferrite. × 100.

FIG. 235.—Malleable cast iron, Blackheart, in which precipitation of carbon is incomplete. Graphite surrounded by ferrite in a groundmass of pearlite. × 100.

FIG. 236.—Malleable cast iron, European or Réaumur. Pearlite. × 250.

FIGS. 237 to 240.—Structure of a specimen of European malleable cast iron from centre to outside.

FIG. 237.—Precipitation of graphite from cementite in the centre, giving graphite, ferrite and pearlite. × 250.

FIG. 238.—Near centre. Pearlite with traces of graphite. × 100.

FIG. 233.

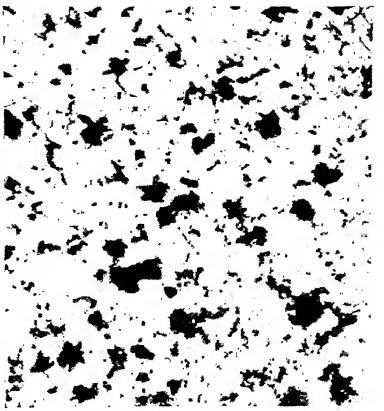

FIG. 234.

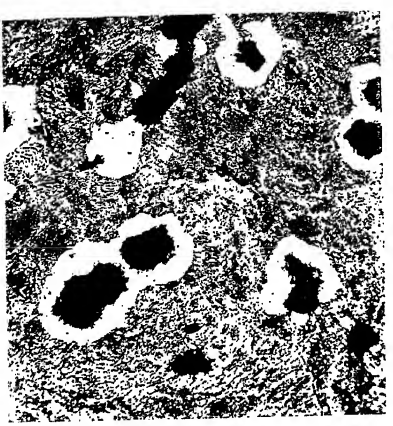

FIG. 235.

FIG. 236.

FIG. 237.

FIG. 238.

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PLATE XLVI.

FIG. 239.

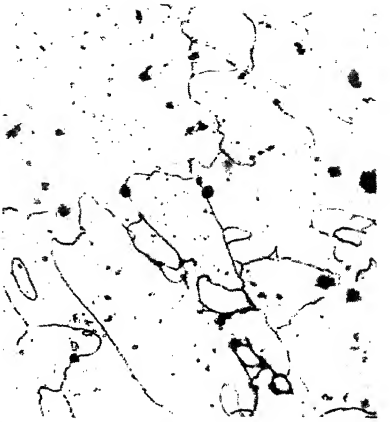


FIG. 240.

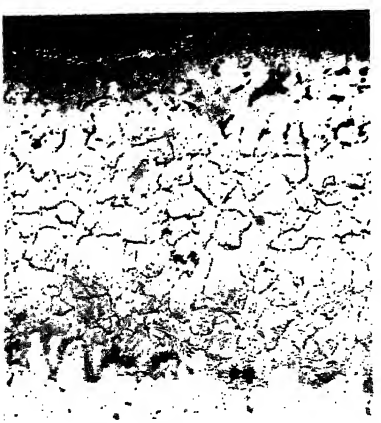
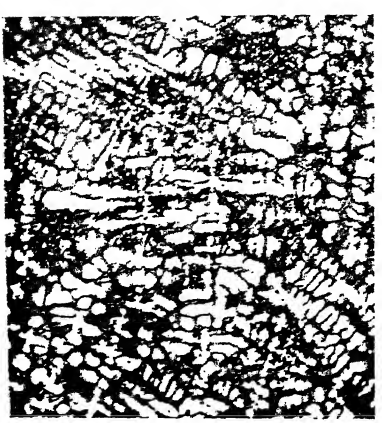
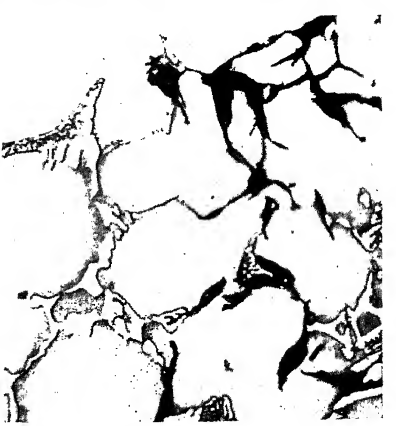


FIG. 241.

FIG. 242.





All etched with nitric acid in alcohol.

FIGS. 239–240.—Structure of a specimen of European malleable cast iron (continued).

FIG. 239.—Between central portion and decarburised edge. Coarse pearlite. × 250.

FIG. 240.—Decarburised edge. Chiefly ferrite. × 250.

FIG. 241.—Blackheart malleable cast iron. A layer of pearlite occurring in the ferrite parallel to and near the decarburised and oxidised edge.

A probable explanation is that the ferrite outside is produced by decarburisation of the skin, while that inside is produced by deposition of graphite, leaving an intermediate layer in which the combined carbon, reduced by decarburisation, is insufficient to cause precipitation of the graphite. × 50.

FIG. 242.—Pearlitic structure of a grey cast iron cylinder. × 250.

FIG. 243.—Austenitic cast iron (non-magnetic), containing 10 per cent. of nickel and 5 per cent. of manganese, showing dendritic structure. × 100.

FIG. 244.—The same material as in Fig. 243. × 1000.

CHAPTER XII

THE EFFECT OF IMPURITIES IN COPPER

THE purest form of copper commercially obtainable is cathode copper, which consists of a parallel growth of crystals, frequently twinned if a high current density has been used in deposition (Fig. 254). When remelted and cast this usually contains traces of oxygen in the form of cuprous oxide. Globules of cuprous oxide are visible in pure coppers in Figs. 53 and 54. Oxygen-free high-conductivity copper is cast, or sintered from powder, under conditions which preclude the absorption of oxygen. Best-selected copper is not electrolytically refined, but special precautions are taken to keep impurities as low as possible.

Unrefined copper, such as Chili bar, contains not less than 97 per cent. of copper, and is free from objectionable impurities which cannot be removed by the refining process. The impurities commonly present are arsenic, antimony, iron, sulphur, oxygen and traces of bismuth. The refining process consists of melting the copper in a reverberatory furnace in an oxidising atmosphere, in order to oxidise the impurities which are then volatilised or pass into the slag. The copper itself is also oxidised, forming Cu_2O, which is soluble in molten copper. The oxide is removed by covering the molten metal with anthracite dust, and stirring vigorously with long wooden poles. If the "poling" has not been carried far enough and excess of cuprous oxide remains in the copper when it is cast, the metal is brittle when hot and when cold, it breaks with a granular brick-red fracture, and is known as dry copper. When cast in an open rectangular mould a longitudinal furrow is formed on the surface of the metal as it sets. The structure of under-poled copper is shown in Fig. 249.

At a later stage of poling a sample taken from the furnace,

and cast in an open mould, solidifies with a flat surface. At this stage the copper is tough and malleable in the highest degree: it is said to be at tough pitch. It breaks with a close-grained salmon-red fracture, and under the microscope shows polyhedral grains with rather thick grain boundaries and numerous particles of oxide or oxidised impurities (Fig. 248). If poling has been carried so far that all the oxygen is removed, the metal on casting shows a longitudinal ridge. It is brittle, and when broken shows a yellowish or pale-

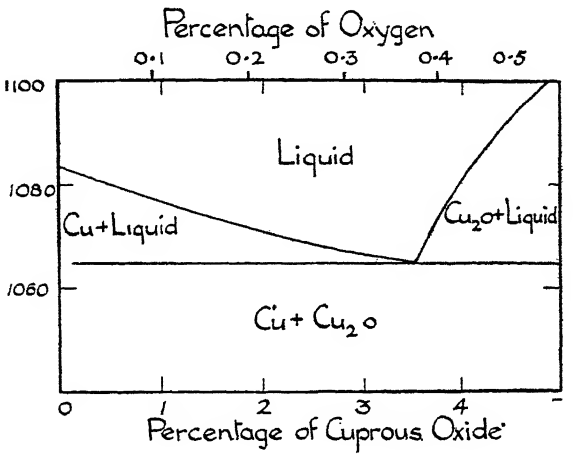


FIG. 245.—Constitutional Diagram of the System Copper–Cuprous Oxide. (*Heyn.*)

coloured uneven fracture disclosing cavities formed by the liberation, at the moment of solidification, of gases dissolved in the molten copper. The brittleness in this case is due to the presence of small quantities of impurities in the unoxidised condition remaining in solid solution in the copper and forming a network round the dendrites of nearly pure copper which solidifies first (Fig. 250).

Effect of Oxygen.—Cuprous oxide (Cu_2O, containing 11·2 per cent. of oxygen) is soluble in molten copper, but only very slightly soluble in solid copper. On solidification it is deposited as a eutectic of Cu_2O and copper containing 3·5 per cent. of Cu_2O (*i.e.* 0·39 per cent. of oxygen), which

freezes at 1065° C., 18° below the freezing point of copper (see diagram, Fig. 245).

The cuprous oxide is of a sky-blue colour and is easily recognised in the unetched specimen (Fig. 255). Slow cooling or annealing causes the granular eutectic to coalesce into globules of Cu_2O.

The effect of oxygen, as has been pointed out, is to make the copper "dry," *i.e.* to reduce its ductility and make it brittle when hot and when cold. Pure electrolytic copper should not contain more than about 0·03 per cent. of oxygen; other commercial coppers usually contain 0·05 to 0·15 per cent. of oxygen.

The small quantity of oxygen which copper normally contains is a source of injury to the metal when it is annealed in a reducing atmosphere. Reducing gases diffuse into the metal and react with the globules of cuprous oxide; hydrogen, for example, will diffuse in far more rapidly than the water vapour formed will diffuse out. Considerable pressure may thus be developed and extensive cracks produced in the metal (Figs. 256, 257).

This action, known as the "gassing" of copper, which ruins the metal for future use or treatment (except remelting) may be avoided by annealing in an oxidising atmosphere and not permitting even momentary contact with reducing gases. Provided there is no objection from the point of view of its effect on the electrical conductivity, the danger of gassing may be eliminated in pure copper by totally removing cuprous oxide by the addition of excess of a deoxidising agent, such as zinc, manganese or aluminium. These additions all form solid solutions with copper and exert only a very slight hardening effect, if present only in small amounts.

Effect of Arsenic.—Copper can retain in solid solution about 7·25 per cent. of arsenic and this solubility changes very little with fall in temperature. Between 7¼ and 21 per cent. the alloys consist of grains of α solid solution in a groundmass of eutectic; from 21 to 28 per cent., they show the

β constituent (possibly Cu_3As) embedded in eutectic (see diagram, Fig. 246).

Arsenic is present in most commercial copper in small traces. Its most pronounced effect is in lowering the electrical conductivity. From 0·35 to 0·55 per cent. of arsenic is purposely introduced into copper for locomotive fire-box plates, to increase its tenacity (especially at elevated temperatures) without sensibly reducing its ductility.

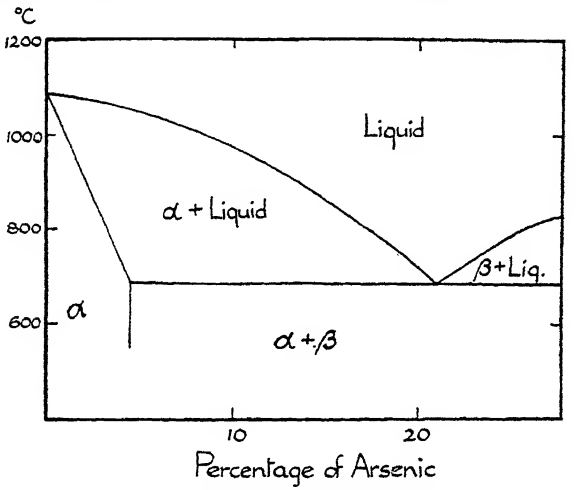


FIG. 246.—Constitutional Diagram of the Arsenic–Copper Alloys. (*Bengough and Hill.*)

A more recent determination of the solubility of arsenic in copper (*Hanson and Marryat*) places the limit of the *a* solution at 7·25 per cent. arsenic.

The constitutional diagram shows that there is a large range of solidification between liquidus and solidus. This gives rise in a casting to a "cored" structure in which the centres of the primary grains consist of almost pure copper, surrounded by grain boundaries of an arsenic-rich solid solution, which may in cases of very rapid cooling contain some eutectic (Fig. 251). On annealing this material diffusion occurs and the structure shows the homogeneous solid solution. Uniformity of the structure is promoted by rolling followed by annealing. Tough pitch arsenical copper contains 0·1 to 0·2 per cent. of oxygen and is damaged by annealing in reducing atmospheres.

Effect of Antimony.—Antimony in such quantities as occur in commercial copper forms a solid solution the range of solidification of which is as great as that of the arsenic-copper alloys. The structure of the quickly cooled metal is therefore similar, showing grains of almost pure copper with antimony-rich grain boundaries. Annealed copper will retain 10 per cent. of antimony in solid solution.

Small amounts of antimony are as effective as arsenic in strengthening copper at 250° C. and the addition of both antimony and arsenic results in a greater improvement. The

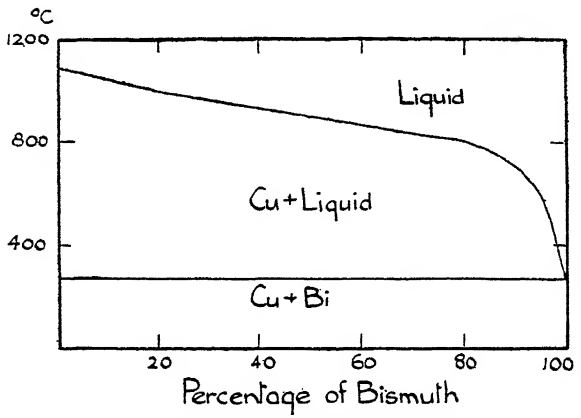


FIG. 247.—Constitutional Diagram of the Bismuth–Copper Alloys. (*Jeriomin.*)

effect of antimony in reducing electrical conductivity is very considerable but it is only approximately half as deleterious in this respect as arsenic. The simultaneous presence of oxygen counteracts the influence of antimony, possibly on account of the formation of an insoluble antimonate of copper which removes antimony from the solid solution.

Effect of Bismuth.—Bismuth exerts a more injurious effect on copper than any other impurity. A very small quantity makes it brittle, and induces weakness, especially at high temperatures. It greatly reduces electrical conductivity.

Although copper and bismuth are completely soluble in the liquid state, they are almost completely insoluble in the solid condition: they form a eutectic containing only 0·2 per

cent. of copper with a melting point less than 1° C. below that of bismuth (see diagram, Fig. 247).

Thus each crystal grain of copper which separates from the liquid containing bismuth is surrounded by a weak and brittle envelope of almost pure metallic bismuth (Fig. 252). Fracture readily occurs through these films, which at temperatures above 268° C. are liquid. If an alloy with 0·5 per cent. of bismuth is pounded up, ductile crystals of pure copper can be separated. In copper containing 0·005 per cent. of bismuth or less the bismuth appears as small scattered particles.

Effect of Lead.—Lead occurs in solid copper in globules or in films surrounding the crystal grains; its action is similar to that of bismuth, and it forms a eutectic containing less than 0·1 per cent. of copper, with a melting point 1° C. below that of lead. The two metals are practically insoluble in one another in the solid state, and are not completely miscible in the liquid state.

Effect of Silicon.—Silicon is sometimes used as a deoxidiser for copper, any excess passing into solid solution. It has a smaller effect on electrical conductivity than most deoxidisers. Copper can retain up to about 4 per cent. of silicon in solid solution at atmospheric temperature. The properties of silicon–copper alloys are dealt with later.

Effect of Phosphorus.—This is a powerful deoxidiser, but even a trace remaining has a bad effect on the conductivity, 0·1 per cent. reducing it to half that of pure copper. Phosphorus in small amounts increases the tensile strength of copper at atmospheric and at raised temperatures, and improves the fatigue limit without impairing toughness; but larger quantities render copper very hard and brittle. Copper and phosphorus form Cu_3P, which is soluble in copper to the extent of 1·2 per cent. at 705° and 0·5 per cent. at 200°, and forms a eutectic at 8·2 per cent. of phosphorus.

Commercial phosphor–copper contains 10 or 15 per cent. of phosphorus and consists of Cu_3P and eutectic. More than

15 per cent. of phosphorus cannot be introduced into the alloy at atmospheric pressure.

Mechanical Properties.—The low resistance to stress offered by pure copper, particularly the absence of an elastic limit in the annealed metal, is a disadvantage for many engineering purposes. The elastic limit of arsenical copper, which is used when greater strength is required, is also very low but extensive investigations have been made by the British Non-Ferrous Metals Research Association to determine how far it is possible by alloying, cold-work and heat treatment, to obtain copper of improved elastic properties.* While not unduly hard at atmospheric temperature, the metal should retain a sufficient elastic limit at temperatures which may be reached in service (when used, for example, as firebox plates) to prevent permanent deformation under low stresses. In this connection the effect of small amounts of a wide range of other elements on the properties of copper has been examined. The micro-structure of all these alloys in the rolled and annealed condition is the same as that of pure copper, but their recrystalising temperatures after cold-working are greatly affected by composition. The typical structure of rolled and annealed copper is evident in Fig. 256, and the sequence of changes on recrystallisation are exactly similar to those undergone by a brass (Figs. 263 to 267). Silver, iron, tin, manganese and silicon raise the softening temperature of cold-worked copper to a greater extent than does arsenic, but only by the addition of silver are the improved elastic properties at raised temperatures gained without appreciable increase in hardness at atmospheric temperature. A very small addition of silver is sufficient, and the great advantage of the presence of 0·05 per cent. of silver in arsenical copper has been demonstrated after suitable mechanical and thermal treatment. The solubility of silver in copper is 0·7 per cent. at 400° C. and decreases rapidly with fall in temperature with probable values

* *Journal of the Institute of Metals*, 1929, (2), vol. xlii, p. 221; 1932, (1), vol. xlviii, p. 69; 1937 (1), vol. lx, p. 109.

of 0·1 per cent. at 250° C. and almost nil at atmospheric temperature.* It thus seems likely that the presence of silver confers on arsenical copper a capacity for temper-hardening.

A systematic research dealing with the effects produced on copper by small additions of other elements has been carried out at the National Physical Laboratory and valuable reports have been published.†

Practical Notes

Polishing of copper requires very great care. It may be carried out with diamantine on a slow-running block, followed by hand polishing with metal polish on selvyt or on chamois leather (see p. 12), the specimen finally being freed from grease by dipping in caustic soda solution. After polishing with some metal polishes, the more convenient process of lightly rubbing the specimen on selvyt soaked with benzene or acetone may be found sufficient. Copper containing appreciable amounts of impurity is generally easier to polish on account of its greater hardness.

Separate polishing blocks should be kept for steel and for copper alloys. When a steel specimen is polished on a pad previously used for copper alloys, a film of copper is deposited on the surface of the steel if the diamantine contains any free acid. If a composite specimen of steel and copper has to be polished (*e.g.* a steel section protected by electro-deposited copper, p. 17), precautions may be taken, if found necessary, to free the diamantine from traces of acid by shaking it up with water, allowing it to settle, and decanting off the liquid.

Etching.—The most satisfactory results are obtained with a 20 per cent. solution of 0·880 ammonia to which 10 per cent. of ammonium persulphate has been added.

A 10 per cent. solution of ammonium persulphate may be used alone, but ammonia (unless aided by the oxidising action

* D. Stockdale: "The Solid Solutions of the Copper–Silver System," *Journal of the Institute of Metals*, 1931, (1), vol. xlv, p. 127.

† Summarised in "The Effect of Impurities on Copper," by S. L. Archbutt and W. E. Prytherch. Published by the British Non-Ferrous Metals Research Association, 1937.

of the atmosphere as in polish attack) will not etch copper. An oxidising agent must always be added: hydrogen peroxide may be used, but it is less satisfactory than ammonium persulphate.

The time of etching depends largely on the purity of the material under examination.

Polish attack may be practised by rubbing the specimen very lightly on a parchment pad wetted with 5 per cent. ammonia for a few minutes. Too great a pressure or too prolonged an attack rounds off the edges of the grains and broadens the boundaries. It is more difficult to avoid this effect if a soft pad (*e.g.* selvyt) is used.

To detect the presence of inclusions, oxide, lead, bismuth, etc., it is desirable also to examine the unetched surface; but to avoid misleading structures due to flow of metal in polishing it is best to etch the specimen after preparation in the usual way, and then to give it a final light polishing before examination of the unetched surface.

CHAPTER XIII

THE STRUCTURE AND PROPERTIES OF ALLOYS OF COPPER WITH ZINC, TIN, SILICON, ALUMINIUM AND NICKEL

THE alloys of copper may be endowed with a wide range of properties by varying their composition and the mechanical and heat treatment to which they are subjected. For this reason they probably rank next to steel in importance to the engineer.

The alloys rich in copper have certain points of resemblance from the micrographical point of view. Reasons for this have been briefly considered in the section on Alloys (p. 78). On account of the number of intermediate phases the constitutional diagrams of some copper alloy-systems become very complicated, but, in general, the alloys which are of industrial importance (except for special purposes) contain only the α constituent or α together with a moderate amount of β.

In accordance with the recommendation of a Committee of the Institute of Metals on the Systematic Nomenclature of Alloys,* it is desirable to denote any alloy by the names of its component metals placed in order of increasing importance from the point of view of chemical composition by weight. Thus, brass containing less than 50 per cent. of zinc is referred to as a zinc–copper alloy.

Zinc–Copper Alloys. The Brasses

The important alloys of copper and zinc from an industrial point of view are all comprised within the limits of composition 0–50 per cent. of zinc. That portion of the constitutional diagram which refers to these alloys is given in Fig. 260.

* *Journal of the Institute of Metals*, 1914, (1), vol. xi, p. 45.

Figs. 248 to 252 etched with ammonia and ammonium persulphate.

FIG. 248.—Tough ingot copper, consisting of grains of copper, and globules chiefly of cuprous oxide. × 50.

FIG. 249.—Underpoled copper containing 0·3 per cent. of oxygen, showing dendrites of copper surrounded by the copper–cuprous oxide eutectic. × 100.

FIG. 250.—Overpoled copper, showing dendrites of copper surrounded by solid solution rich in impurities. × 100.

FIG. 251.—Cast copper containing 0·5 per cent. of arsenic, consisting of grains of copper containing some arsenic in solution surrounded by solid solution rich in arsenic. × 100.

FIG. 252.—Cast copper containing 0·1 per cent. of bismuth: the bismuth separates along the grain boundaries. × 100.

FIG. 253.—Cast aluminium–copper alloy containing copper 94·5 per cent., aluminium 5 per cent. and phosphorus 0·5 per cent.: the black etching dendrites contain phosphorus in solid solution and are surrounded by a solid solution rich in phosphorus.

Etched with acid ferric chloride solution. × 100.

FIG. 248.

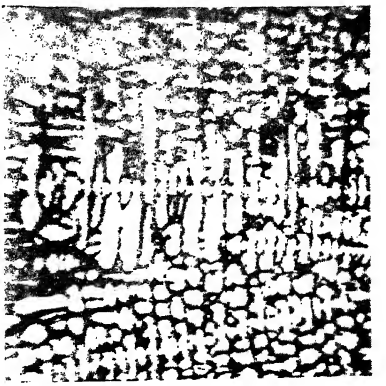


FIG. 249.

FIG. 250.

FIG. 251.

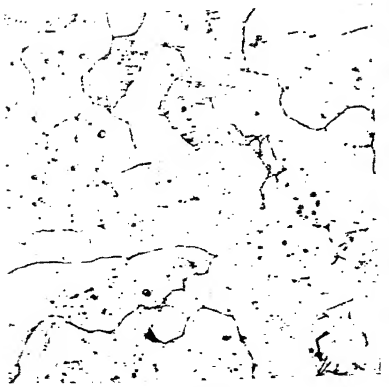


FIG. 252.

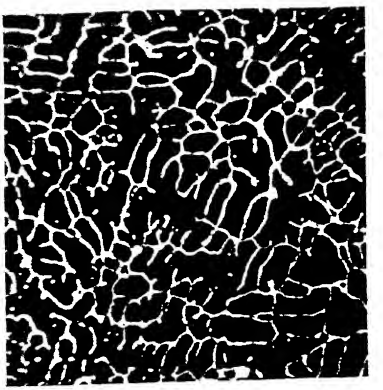


FIG. 253.

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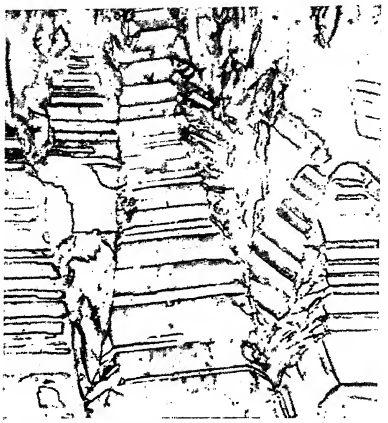


FIG. 254.

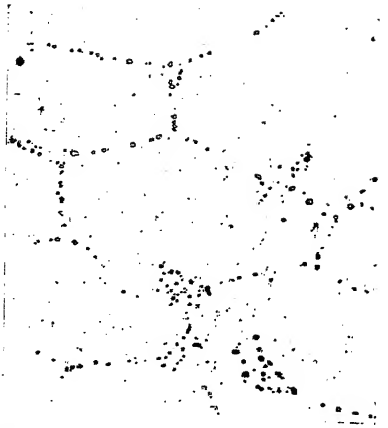


FIG. 255.

FIG. 256.

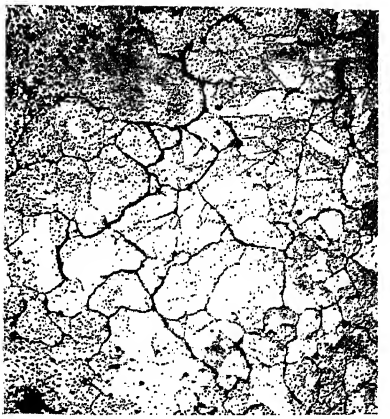
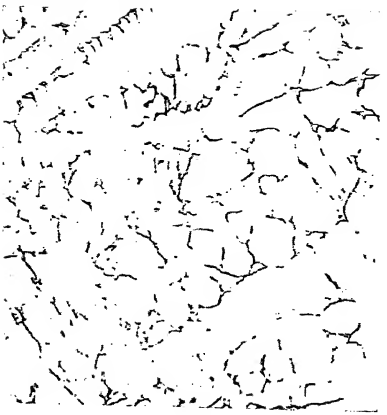


FIG. 257.



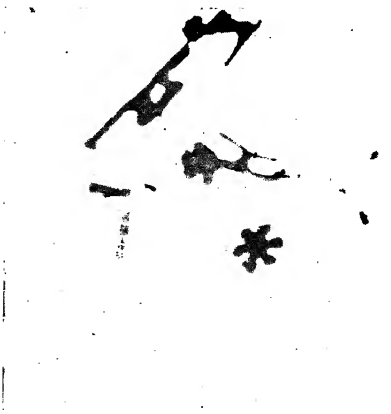


FIG. 254.—Electro-deposited copper, showing twinning.
Etched with ammoniacal solution of ammonium persulphate (polish attack). × 250.

FIG. 255.—Copper containing 0·08 per cent. of oxygen, as cast, consisting of grains of copper and globules of cuprous oxide.
Unetched. × 100.

FIG. 256.—Copper rod, which has been annealed in a reducing atmosphere, showing intercrystalline cracks.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 257.—Copper rod which has been annealed in a reducing atmosphere, showing intercrystalline cracks.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 258.—Cast brass containing copper 71, zinc 27 and aluminium 2 per cent., showing the α solid solution with interdendritic β. The structure is equivalent to that of a 65 : 35 copper–zinc alloy.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 259.—Inclusions of zinc oxide in cast 70 : 30 brass.
Unetched. × 500.

The addition of zinc to copper results in the formation of a series of solid solutions which, in accordance with usual practice, are referred to in order of diminishing copper content as the α, β, γ, etc., constituents. The diagram may be summarised as follows :—

Percentage composition.		Constituent just below the freezing point.	Constituent after slow cooling to atmosphere temperature.
Copper.	Zinc.		
100 to 67·5	0 to 32·5	α	α
67·5 ,, 63	32·5 ,, 37	$\alpha + \beta$	α
63 ,, 61	37 ,, 39	β	α
61 ,, 55·5	39 ,, 45·5	β	$\alpha + \beta'$
55·5 ,, 50	45·5 ,, 50	β	β'
50 ,, 43·5	50 ,, 56·5	β	$\beta' + \gamma$
43·5 ,, 41·5	56·5 ,, 58·5	$\beta + \gamma$	$\beta' + \gamma$

These limits, of course, refer to conditions of equilibrium produced by very slow cooling or prolonged annealing: the constituents present after more rapid cooling can be surmised by taking into account the changes undergone, but possibly not carried to completion, by the alloy during cooling from the freezing point.

Thermal curves and measurements of electrical resistivity indicate that the β constituent undergoes a change at about 470° C. The type of crystal lattice is the same above and below 470° C. but the distribution of the zinc atoms among the copper atoms within the lattice is altered. At temperatures above 470° C. the copper and zinc occupy corners and centres of a body-centred cubic lattice at random. Below 470° C. they begin to segregate, one set going to the corners and another to the centres. This distribution of atoms in regularly selected positions of the underlying phase pattern is termed a superlattice, and the change a disorder-order transformation. Such a change affects the electrical resistivity and the true specific heat at the temperature of transformation, giving rise to a thermal arrest point*. In β-brass a superlattice cannot exist above 470° C.; below that temperature the rate of

* See "Atomic Arrangement in Metals and Alloys," by W. L. Bragg, *Journa of the Institute of Metals*, 1935, (1), vol. lvi, p. 275.

change to the ordered condition rapidly diminishes with falling temperature. If this rate is high at the critical temperature, as in β-brass, the structure is not prevented from becoming ordered even when the alloy is quenched. If the critical temperature for the formation of a superlattice is low, the possibility of atomic rearrangement ceases before it is reached, and the structure is permanently disordered. If it is as high as the melting point, the lattice is completely ordered from

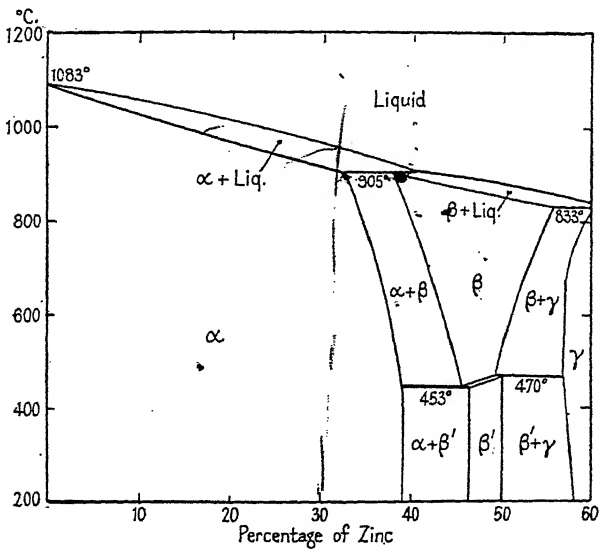


FIG. 260.—Constitutional Diagram of the Zinc–Copper Alloys. (*Shepherd, Hudson, Haughton and Griffiths, Genders and Bailey, and others.*)

the freezing point downwards, a structure associated with the well-defined intermetallic compounds, for example NiAl. The change to the ordered condition cannot be suppressed in β-brass, and the only form which can exist at atmospheric temperatures is β', but for ordinary purposes it is usual to refer to the constituent as β.

There is a certain connection between the properties and the microstructure which may be expressed in general terms.

1. The tensile strength increases with increase in zinc content, rises somewhat abruptly with the appearance of β, and reaches a maximum at a composition corresponding

roughly to equal parts of α and β; it falls off rapidly at the appearance of the γ constituent (Fig. 261).

2. Elongation rises to a maximum and begins to fall again before the composition reaches the limit of the α solution; it falls considerably as the amount of β increases, and is very small in the presence of γ (Fig. 261).

3. The α constituent shows the greatest resistance to shock: this is diminished by the presence of β, and the alloy becomes extremely brittle when γ is present.

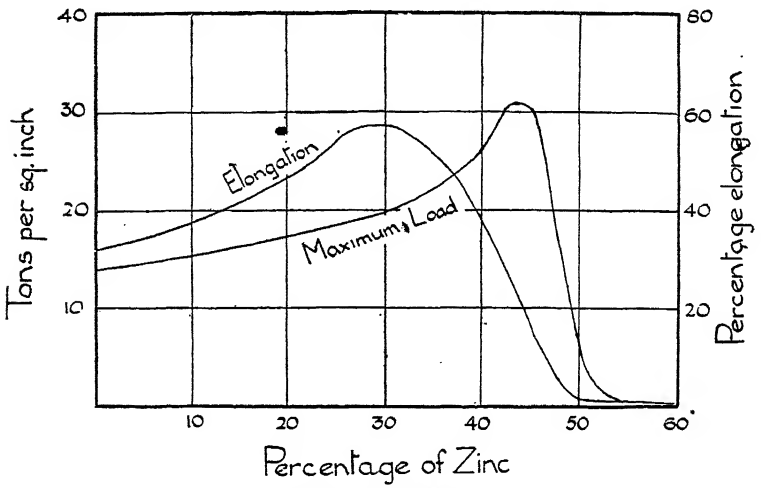


FIG. 261.—Effect of Composition on the Mechanical Properties of the Annealed Brasses. (*Charpy.*)

4. Hardness is greatly increased by the presence of β and still further when γ appears.

5. Alloys containing α only are specially suitable for working cold, and may be rolled hot or cold; those containing α and β will suffer very little deformation in the cold without rupture and may only be rolled hot. The β constituent may also be forged, rolled or extruded hot, but alloys containing γ should invariably be avoided for any mechanical treatment.

The brasses of industrial importance are often designated by their copper and zinc content.

85 : 15 Brass.—Gilding metal. This is used for ornaments

and for cheap jewellery which is to be gilded: it withstands cold-work, cupping, etc. On account of the range of solidification, the cast material has a dendritic structure. If cooled very slowly or annealed, diffusion takes place, yielding polyhedral grains of uniform composition. The process of diffusion is assisted by mechanical deformation of the grains by hot- or cold-work followed by annealing. The changes which occur on rolling and annealing are similar to those described for 70 : 30 brass.

70 : 30 Brass.—This alloy, which is used widely for tubes, sheets and wire, also shows a dendritic structure of the α solid solution when chill cast. The β constituent does not begin to appear in the cast structure until the zinc exceeds 32 per cent. except in the presence of an additional element like aluminium or tin (Fig. 258). After annealing, the alloy consists of homogeneous α solid solution, and it is specially suitable for cold-working. To withstand this treatment, especially drawing, it is necessary that the brass should be perfectly sound and free from deleterious impurities. Since high grade 70 : 30 brass is usually made from the purest copper and zinc available without admixture of any but the cleanest scrap, these impurities are chiefly inclusions of dross (oxides or silicates) or charcoal (Fig. 259). Such inclusions, if present, frequently lead to failure of the material during manufacture or in use. They become entrapped in the solidifying metal, either by splashing or by rapid solidification in moulds of small cross section. It is a frequent custom in casting brass for drawing into rod to employ very long moulds of very small cross section, in order to minimise subsequent mechanical treatment. Ingots made in such moulds are most liable to contain inclusions and to show piping to a great depth, resulting in central unsoundness over a considerable length of the ingot. To ensure soundness it is necessary to cast in a mould such that the cross section is large enough to give relatively slow cooling. The mould and stream of molten metal should be so arranged as to avoid splashing, and the

dimensions of the mould and speed of pouring should be such as to result in the ingot solidifying from bottom upwards.

The effect of cold-work on the microstructure is to break down the crystal grains by plastic deformation, and so crush them into a confused mass of crystalline débris (Figs. 263, 269). Annealing after cold-work results in recrystallisation and subsequent crystal growth.

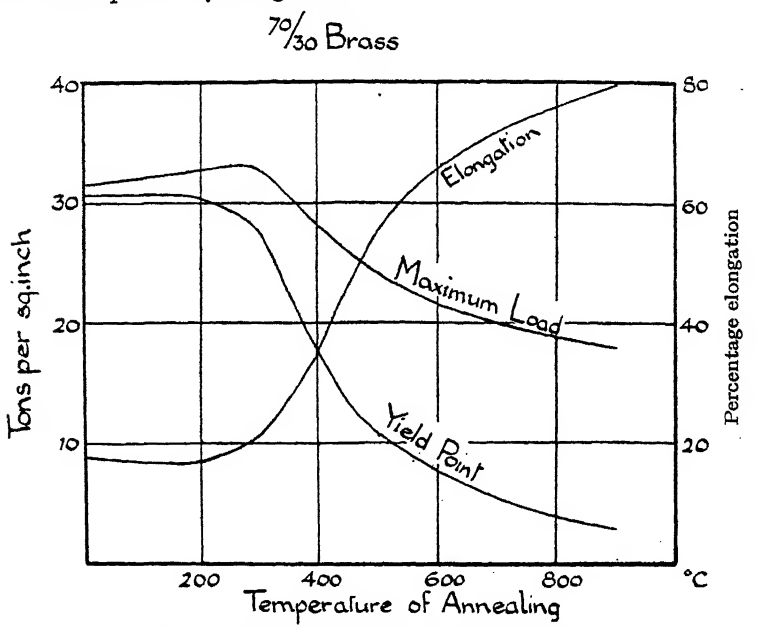


FIG. 262.—Effect of Annealing ($\frac{1}{2}$ hr.) on the Properties of Cold-rolled 70 : 30 Brass. (*Bengough and Hudson.*)

For typical cold-rolled 70 : 30 brass of Brinell hardness about 165 (Fig. 263) annealed for $\frac{1}{2}$ hour at gradually increasing temperatures, there is first a slight rise, and after annealing above 300° C. a slight fall, in the hardness and tensile strength (see diagram, Fig. 262). Meanwhile there is no visible change in the microstructure. The elongation is unaffected up to 300° C., but between 300° and 400° C. shows a rapid increase : this is coincident with the period of recrystallisation. The structure at this point is distinctly finer than that of the cold-worked material (Fig. 264). Above this temperature

crystal growth proceeds (Figs. 265–267) and the new grains show pronounced twinning. On annealing at temperatures up to about 600° C. there is a progressive fall in tensile strength and rise in elongation; from 600° to 750° C. these properties remain approximately constant, subsequently at higher temperatures with the very large crystal growth characteristic of over-annealed brass there is a further fall in tensile strength, accompanied, when the metal is "burnt," by a sudden fall in elongation. Over-annealed brass may by careful treatment be cold-worked, re-annealed and so refined in structure. Burnt brass is extremely friable and useless unless remelted. This effect is produced when brass is annealed at temperatures close to the solidus; it is probably due in part to volatilisation of zinc, and is certainly accelerated by the presence of lead, which collects into and corrodes the grain boundaries. A pure brass will sustain over-annealing without burning far better than one containing small quantities of impurities.

Burnt 70 : 30 brass consists of very large α-grains showing pits and specks distributed over the surface, and distinct grain boundaries.

Season Cracking.—Brasses of a wide range of composition (including 70 : 30 and 60 : 40) are liable to season cracking, which, however, occurs only in material which is maintained in a state of stress either by external constraint or, more commonly, by internal stress. Season cracks almost invariably follow an intercrystalline path (Fig. 268).

A suitably controlled low-temperature annealing (below 300° C.), which removes internal stress but has little or no effect on the hardness, appears to be the most efficient safeguard against failure by season cracking. The mercurous nitrate test for the detection of injurious internal stress in cold-worked copper alloys is described in the notes at the end of this chapter.

60 : 40 Brass.—Muntz metal. The molten metal on cooling begins to freeze at about 905° C., and dendrites of the β solution are formed. With sufficiently slow cooling

through the range of solidification the alloy consists of homogeneous β constituent when just solid, but, on cooling, this solution retains less copper and at 770° C. the α constituent separates from the homogeneous β and increases in amount as the temperature falls. The structure on reaching atmospheric temperature is therefore a mixture of α and β, the relative proportions of which may be controlled to some extent by the rate of cooling (Fig. 271). For example, a thin section of 60 : 40 brass quenched from 800° C. consists of homogeneous β; with a larger section it is impossible to suppress completely the separation of α, but a specimen rapidly cooled from this temperature always contains more β than a specimen more slowly cooled. These microstructural characteristics are accompanied by changes in mechanical properties which can be deduced from the known hardness and brittleness of the β constituent and the softness and ductility of the α constituent. Hot-rolled 60 : 40 brass, the rolling of which has been stopped above 700° C., shows a uniform structure in longitudinal and transverse directions. After the separation of α has begun, the α and β constituents are each elongated in the direction of rolling, giving the normal structure of rolled 60 : 40 brass (Fig. 272). The lower the temperature of finishing the smaller will be the grain size. If, however, rolling is continued much below 600° C., recrystallisation does not keep pace with the deformation and the metal is cold-worked.

50 : 50 Brass.—Brazing solder. This alloy, if cooled sufficiently slowly through the range of solidification, consists of homogeneous β solution, which, however, may decompose on cooling if the copper content is less than 50 per cent. At atmospheric temperature the β solution will retain a maximum of just 50 per cent. of zinc if no impurities are present, but any excess of zinc over 50 per cent. causes the separation of the γ constituent, which increases in amount as the temperature falls. Its presence renders the alloy extremely hard and brittle.

Special Brasses.—Small proportions of other metals are sometimes added to zinc–copper alloys for special purposes for which increased strength, hardness or resistance to corrosion is required. Iron, aluminium, and manganese all give commercial alloys of great tensile strength and high resistance to corrosion. As a rule these additions do not involve the formation of a separate constituent. The useful alloys of this type consist of the α, β or α and β solutions, no longer containing copper and zinc only, but modified in composition and in properties by the addition of the special metal. The limits of composition of the α and β solutions are affected, and so also are the proportions present in the microstructure. With respect to this modification of the microstructure, each element may be regarded as playing the part of an equivalent quantity of zinc. Thus in their effect solely on the structure (not on the mechanical properties of the constituents)—

1	part of	manganese	is	approximately	equivalent	to	0·5	part	of zinc.
1	,,	iron	,,	,,	,,	,,	0·9	,,	,,
1	,,	tin	,,	,,	,,	,,	2	parts	,,
1	,,	aluminium	,,	,,	,,	,,	6	,,	,,

Thus an alloy containing 70Cu + 26Zn + 4Al will have, after similar treatment, a similar structure to one containing

$$\frac{26 + (4 \times 6)}{70 + 26 + (4 \times 6)} \times 100 = \frac{50}{120} \times 100 = 41{\cdot}7 \text{ per cent. of zinc.}$$

i.e. substitution of 4 per cent. of aluminium for zinc in 70 : 30 brass gives rise to an $\alpha + \beta$ alloy. Similarly substitution of 3 per cent. of aluminium for zinc in a 60 : 40 brass converts it into an alloy consisting of the β solid solution alone (Fig. 273) while the substitution of 5 per cent. of aluminium for zinc results in the separation of the γ constituent (Fig. 274), and has an exceedingly embrittling effect. The use of about 2 per cent. of aluminium in brasses of different copper contents not only improves the mechanical properties, but secures increased resistance to corrosion, and to oxidation at high temperatures, by the formation of a protective surface film of aluminium oxide.* The structural equivalent of

* See R. Genders, "The Aluminium-Brasses," *Journal of the Institute of Metals*, 1930, (1), vol. xliii, p. 163.

Recrystallisation and grain growth in 70 : 30 brass. All showing the α solid solution.

FIG. 263.—Cold-drawn 70 : 30 brass showing broken-down crystal grains of the α constituent. Brinell hardness 165.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 264.—The same brass heated 3 hrs. at 350° C. Recrystallisation has occurred with refining of the grain size. Brinell hardness 90.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 265.—Cold-drawn 70 : 30 brass annealed ½ hr. at 650° C.
Etched with ammoniacal solution of ammonium persulphate. × 100.

FIG. 266.—Cold-drawn 70 : 30 brass annealed ½ hr. at 750° C.
Etched with acid ferric chloride solution. × 100.

FIG. 267.—Cold-drawn 70 : 30 brass annealed ½ hr. at 850° C.
Etched with acid ferric chloride solution. × 100.

FIG. 268.—"Season cracks" in 70 : 30 brass. The cracks are intercrystalline.
Etched with ammoniacal solution of ammonium persulphate. × 100.

PLATE XLIX.

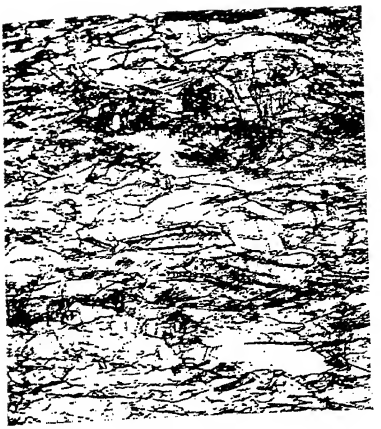


FIG. 263.

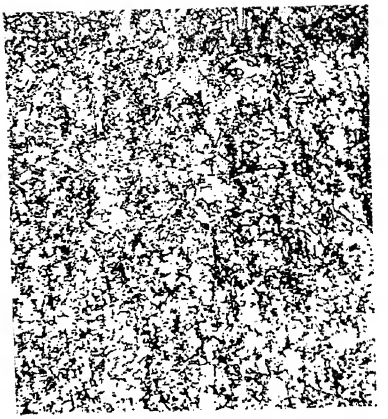


FIG. 264.

FIG. 265.

FIG. 266.

FIG. 267.

FIG. 268.

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PLATE L.

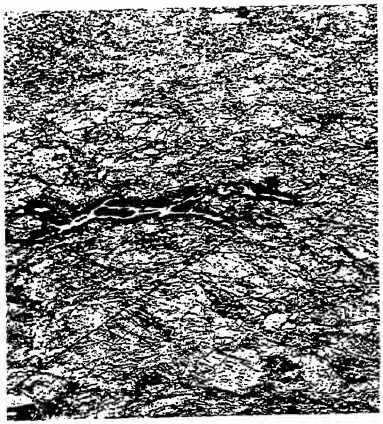


FIG. 269.

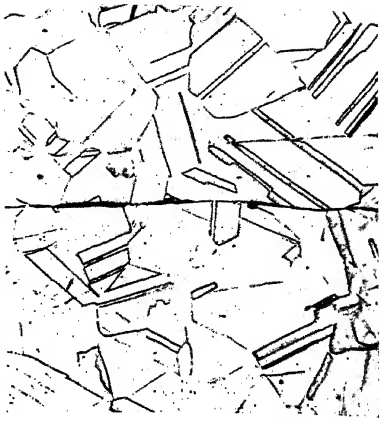


FIG. 270.

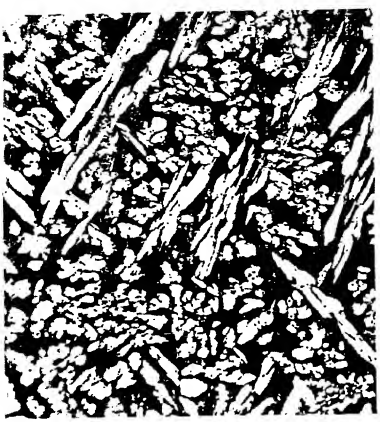


FIG. 271.

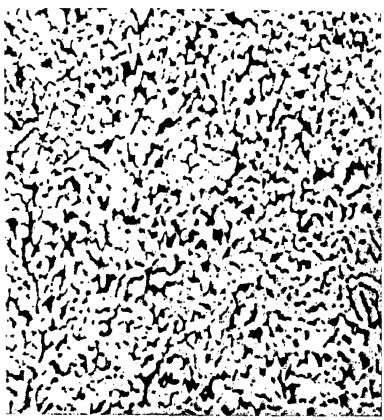
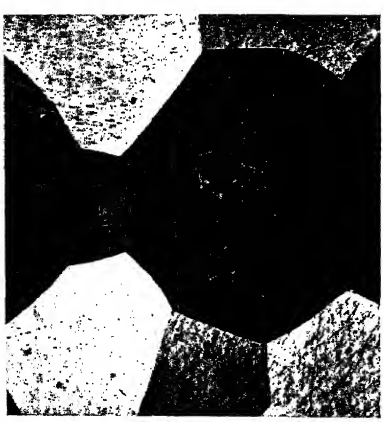
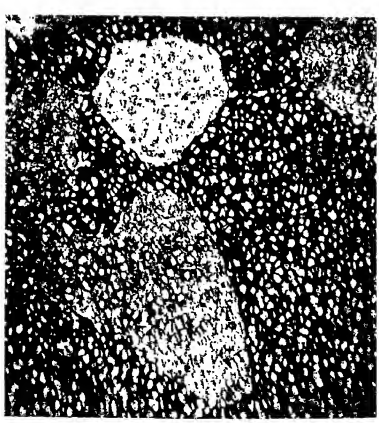


FIG. 272.





FIGS. 269 to 272 etched with ammoniacal solution of ammonium persulphate; Figs. 273 and 274 with acid ferric chloride solution.

FIG. 269.—Inclusion in cold-drawn 70 : 30 brass. × 100.

FIG. 270.—Oxidised discontinuity ("spill") in annealed 70 : 30 brass strip. × 50.

FIG. 271.—Cast 60 : 40 brass, consisting of α and β solid solutions. α light, β dark. × 100.

FIG. 272.—Rolled 60 : 40 brass, transverse section, showing α and β solid solutions. × 100.

FIG. 273.—Brass containing 60 per cent. of copper and 2·8 per cent. of aluminium, annealed, showing the β solid solution only. × 100.

FIG. 274.—Brass containing 60 per cent. of copper and 5 per cent. of aluminium, showing β and γ solid solutions. Light particles of γ in groundmass of β. × 50.

70 : 30 brass is a 76 : 22 : 2 copper–zinc–aluminium alloy. The amount of the special element must never be sufficient to cause the formation of a new deleterious constituent. Thus, the addition of 1 to 1·5 per cent. of tin to 60 : 40 brass gives Naval brass (copper 60, zinc 39, tin 1 per cent.), showing improved resistance to corrosion by sea-water. With larger amounts of tin a constituent is formed in the β solution which is analogous to the δ constituent of the bronzes, and makes the alloy very hard and brittle.

Tin–Copper Alloys. The Bronzes

As in the case of the brasses, the addition of tin to copper results in the formation of a series of solid solutions. The constitutional diagram of tin–copper alloys is very complex, but that part of it which deals with alloys of industrial importance, though not finally established in detail, is reproduced in Fig. 275 and may be summarised as follows :—

Percentage composition.		Constituents just below the freezing point after slow cooling through the range of solidification.	Constituents after slow cooling to atmospheric temperature.
Copper.	Tin.		
100 to 87	0 to 13	α	α
87 ,, 86	13 ,, 14	$\alpha + \beta$	α
86 ,, 78	14 ,, 22	$\alpha + \beta$	$\alpha + \delta$
78 ,, 74	22 ,, 26	$\beta \rightarrow (\alpha + \beta)$	$\alpha + \delta$

The β constituent does not exist in the alloy slowly cooled to ordinary temperatures: this is due to a change occurring at 520° C. whereby β is resolved into α and δ. The α solution is the softest of these constituents; it may be rolled or stamped cold, but hardens under this treatment much more rapidly than α brass. The β solution is harder. The δ constituent has the crystal structure of γ-brass, and to preserve uniformity is now sometimes referred to as γ. It has a narrow range of composition corresponding approximately to the formula $Cu_{31}Sn_8$ and like all intermetallic compounds, is extremely

hard and brittle. The alloys richer in tin, not shown in the diagram, may contain the ϵ constituent (previously known as η) which corresponds to Cu_3Sn (p. 79) and the η solid solution (at one time referred to as ϵ) which approximates to the composition CuSn.

5 per cent. Tin–Copper Alloy.—On cooling from the liquid condition, the α solid solution which first forms contains only about 2 per cent. of tin. Thus the cast metal has a cored

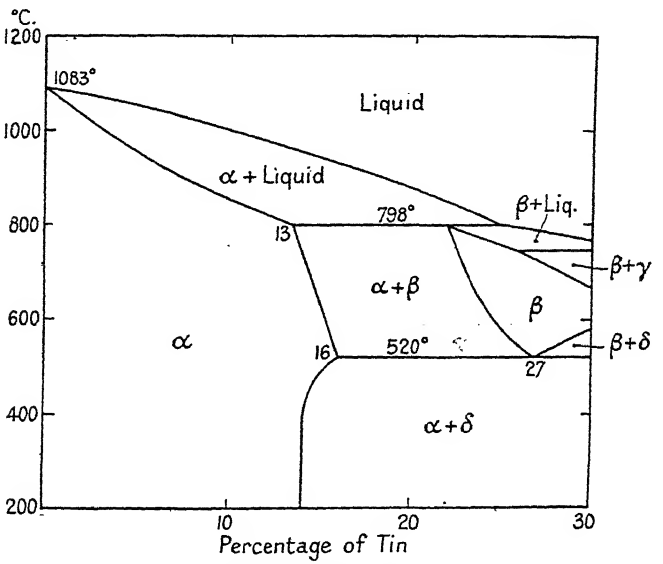


FIG. 275.—Constitutional Diagram of the Tin–Copper Alloys. (*Heycock and Neville, Isihara, Haughton and others.*)

structure (Fig. 278), and the coring is very marked because of the long range between liquidus and solidus; but it may be eliminated by diffusion on cooling more slowly or by annealing.

Any absorption of oxygen occurring during manufacture results in the presence of SnO_2 in the alloy, tending to make it brittle. A deoxidiser such as zinc is therefore frequently added. The addition of zinc, as in coinage bronze (copper 95, tin 4, zinc 1 per cent.), causes no change in the microscopical appearance of the homogeneous α constituent, the zinc, how-

ever, exerting its deoxidising effect in the liquid, and slight hardening effect on the solid solution. The structure of a bronze coin shows marked deformation of the crystals. On annealing recrystallisation takes place with subsequent crystal growth, as in the case of α brass. Twinning is a characteristic feature of the cold-worked and annealed alloy (Fig. 279).

10 per cent. Tin–Copper Alloy.—This is typical of gun-metal, most varieties of which, however, contain a deoxidiser, frequently zinc (*e.g.* Admiralty gun-metal, copper 88, tin 10, zinc 2 per cent.). The structure of the cast material is very dependent on the rate of cooling, both through the range of solidification and below. On account of the wide solidification range of the alloy and the slow rate of diffusion of tin, the apparent solubility limit of the α solution is well below that shown in the diagram. The cast structure is always definitely dendritic and if coring is pronounced, some β solution may be formed at 798° C. This interdendritic β, on cooling, gives rise to the hard δ constituent. On the other hand, after slow cooling or prolonged annealing, the homogeneous α constituent may be produced. A chill-cast gun-metal will therefore be very different in structure and properties from one which has been annealed.

15 per cent. Tin–Copper Alloy.—This is typical of a number of bronzes used as bearing metals, most of which, however, contain a little zinc as a deoxidiser. It is also the approximate composition of bell metal. Immediately after solidification the alloy consists of the α and β constituents. If rapidly cooled, these are preserved (Fig. 280). If slowly cooled, the β is completely broken down below 520° C. into a complex $\alpha + \delta$, the $\alpha + \beta$ structure being replaced by $\alpha + (\alpha + \delta)$ complex in the slowly cooled alloy (Fig. 281). This accounts for the fact that sand castings of this alloy are much harder than chill castings. It also provides the basis of a method of heat treatment, applied in the one case to bells and in the other to bearing metals, by which in the former

case quenching from about 600° C. yields a softer and tougher alloy of better tone, and in the latter case slow cooling from a similar temperature induces the separation of the very hard δ constituent in a comparatively plastic groundmass of α.

Special Bronzes.—Various elements have been added to bronze as deoxidisers; any excess over that required to remove the oxygen is found in the alloy and affects the properties. These deoxidisers include silicon, aluminium, and manganese, but most important of all is phosphorus. Phosphor–bronzes containing less than 9 per cent. of tin and only traces of phosphorus (up to 0·2 per cent.) are suitable for rolling or drawing and have the simple structure of the homogeneous α constituent. They are really very completely deoxidised bronzes. For certain purposes advantage is taken of the increased hardness conferred by the presence of phosphorus in the alloy. Thus alloys with 8 to 10 per cent. of tin and 0·5 per cent. phosphorus are used for valves, while still harder alloys with 10 to 12 per cent. of tin and phosphorus ranging from 0·5 to 1·5 per cent. are used for gearing, bearings, and parts in which excessive wear is to be guarded against. The phosphorus separates as hard particles of Cu_3P associated with the δ constituent in these alloys, enhancing their properties as bearing metals. The two constituents are best distinguished by heat tinting, which colours the phosphide blue, while the δ constituent remains yellow.

Reference must also be made to bronzes containing lead which separates in the solid alloy in globules and films. A small quantity enables the metal to be turned and filed easily, but larger quantities are used for statuary and for bearings. Bearing metals of this type are known as plastic bronzes. Liquation is a serious difficulty in these alloys, but as much as 30 per cent. of lead can be fairly uniformly distributed in an alloy of the composition: copper 64, lead 30, tin 5 and nickel 1 per cent., used as a bearing metal.

Silicon–Copper Alloys. Silicon Bronzes

The constitutional diagram of the silicon–copper alloys (Fig. 276) bears some resemblance to that of the tin–copper alloys, and the structure of the copper-rich alloys of both series is similar. The most important commercial alloy contains about 3·5 per cent. of silicon together with small quantities of zinc, iron and manganese. In the cast condition it shows the hard bluish γ constituent which stands out in high

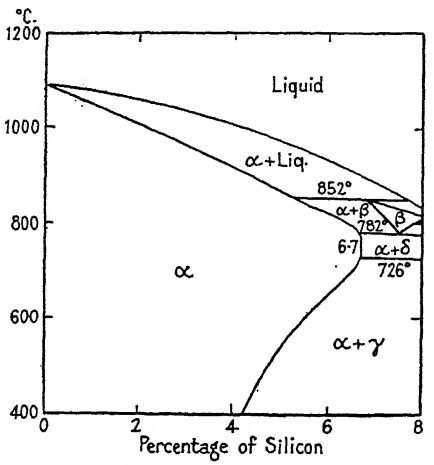


FIG. 276.—Constitutional Diagram of the Silicon–Copper Alloys. (*Smith.*)

relief on the polished surface. The α groundmass, when etched, shows considerable coring, characteristic of a cast alloy with a long freezing range (Fig. 282). The complex silicon bronzes possess properties similar to those of gun-metal.

Silicon bronzes can readily be hot forged, and in this condition have the structure of a uniform solid solution, and good mechanical properties comparable with those of the complex brasses. Some of the alloys are susceptible to heat treatment. The solubility of silicon in copper reaches its maximum value of 6·7 per cent. between 726° and 782° C. and falls to less than 4 per cent. at 350° C. It is therefore possible to harden the quenched alloys by tempering. The addition of aluminium or of zinc reduces the solubility of

silicon, but does not alter the character of the solubility curve, and the complex alloys of silicon–aluminium–copper and silicon–zinc–copper will also undergo temper hardening when suitably treated.

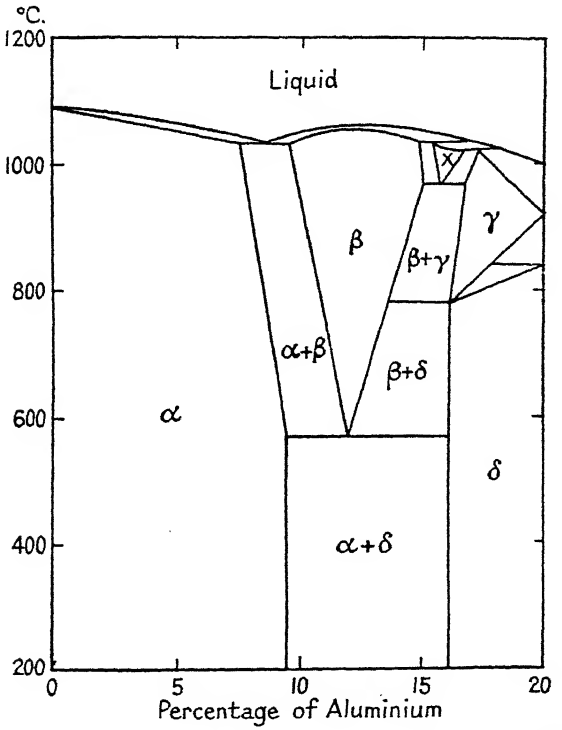


FIG. 277.—Constitutional Diagram of the Aluminium–Copper Alloys. (*Carpenter and Edwards, Andrew, Stockdale, Dowson.*)

Aluminium–Copper Alloys. Aluminium Bronzes

The constitution of the alloys of industrial importance is indicated in the diagram (Fig. 277) and the following table :—

Percentage composition.		Constituents just below the freezing point.	Constituents after slow cooling to atmospheric temperature.
Copper.	Aluminium.		
100 to 92·5	0 to 7·5	α	α
92·5 ,, 91	7·5 ,, 9	$\alpha + \beta$	α
91 ,, 84	9 ,, 16	$\beta \rightarrow (\alpha + \beta)$	$\alpha + \delta$

Etched with acid ferric chloride solution.

FIG. 278.—Bronze containing 5 per cent. of tin as cast, consisting mainly of the α solid solution, with particles of δ. The liquid last to solidify formed interdendritic β, which has subsequently broken down to α (absorbed in the original α grains) + δ (light). × 100.

FIG. 279.—Coinage bronze (copper 95 per cent., tin 4 per cent., zinc 1 per cent.) annealed at 600° C., consisting of the α solid solution showing twinning. × 100.

FIG. 280.—Bronze containing 15·8 per cent. of tin: quenched from 600° C., consisting of α (light) and β (dark). × 100.

FIG. 281.—Bronze containing 15·8 per cent. of tin; heated to 600° C. and slowly cooled, consisting of α (dark) and (α + δ) complex in which δ etches light. Some α from the complex has separated on and been absorbed by the large α grains, leaving them surrounded by a fringe of δ. × 100.

FIG. 282.—Sand-cast silicon–copper alloy (silicon bronze), containing copper 92, silicon 3·5, zinc 2·0, iron 2·0 per cent., showing cored α solid solution with a separation, in the silicon-rich light-etching areas, of particles of the γ solid solution of silicon in copper. × 100.

FIG. 283.—Chill-cast nickel–aluminium–copper alloy (copper 85·5 per cent., aluminium 5·0 per cent., nickel 9·5 per cent.), showing pronounced dendritic structure of nickel-rich dendrites in the α solid solution.

This alloy may be temper-hardened (cf. Figs. 67 and 68). Its tensile strength as cast was 28 tons per sq. inch; as quenched in water after annealing at 900° C., 21 tons per sq. inch (structure, α solid solution); and reheated to 550° C. for twelve hours after quenching 44 tons per sq. inch. × 100.

FIG. 278.

FIG. 279.

FIG. 280.

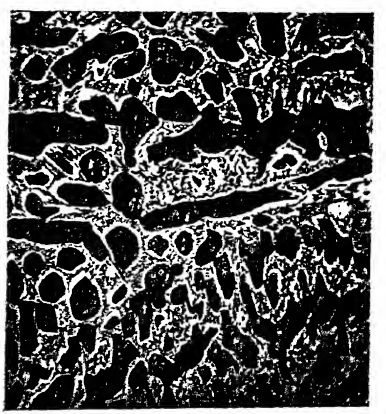


FIG. 281.

FIG. 282.

FIG. 283.

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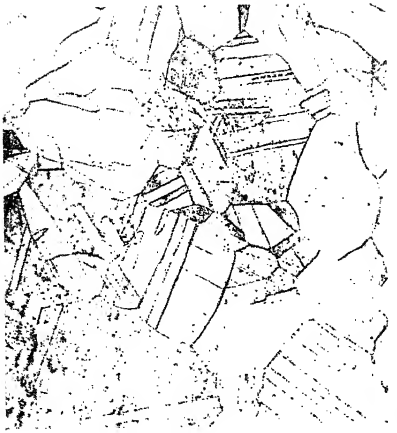

FIG. 284.

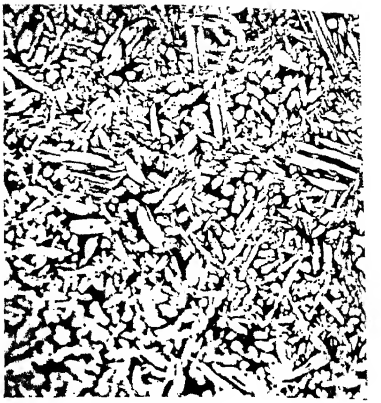

FIG. 285.

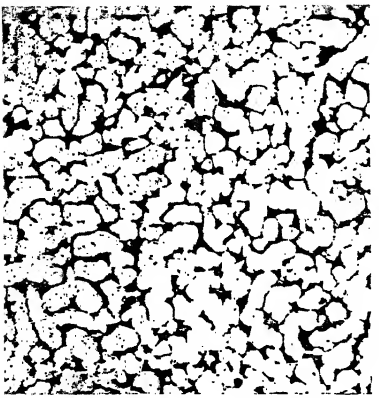

FIG. 286.

FIG. 287.

FIG. 288.

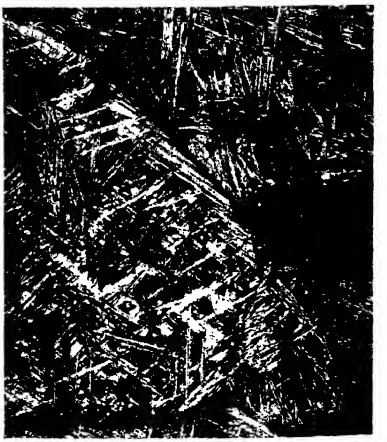

FIG. 289.

Aluminium–copper alloys.

All etched with acid solution of ferric chloride.

FIG. 284.—Alloy containing copper 95 per cent., aluminium 5 per cent. rolled and annealed, consisting of the α solid solution showing twinning. × 100.

FIG. 285.—Alloy containing copper 90 per cent., aluminium 10 per cent. as cast. α (light) and β (dark). × 100.

FIG. 286.—The same alloy (90 : 10) hot-rolled. Transverse section. α and β. × 100.

FIG. 287.—The same alloy (90 : 10) rolled at a lower temperature. Longitudinal section, showing pronounced bands of α and β. × 100.

FIG. 288.—The same alloy (90 : 10) heated to 700° C. and slowly cooled. The β constituent has broken down into the complex ($\alpha + \delta$). α (light), δ (dark). The α is surrounded by a fringe of δ as in the case of the bronze shown in Fig. 281. × 250.

FIG. 289.—The same alloy (90 : 10) heated to 950° C. and quenched in water, showing a martensitic structure produced by the incipient separation of α (light needles) from the β constituent (dark). × 50.

Mechanical properties associated with the structures illustrated.

	Fig. 284.	Fig. 285.	Fig. 286.	Fig. 287.	Fig. 288.	Fig. 289.
Yield point, tons per sq. in.	6	12	18	42	15	35
Maximum load, tons per sq. in.	24	32	38	44	26	54
Elongation per cent. on 2 in.	83	20	30	9	9	2
Impact figure, ft.-lbs., B.S.I. test-piece	130	—	26	—	4	—

Up to 7·5 per cent. of aluminium these alloys consist of homogeneous α solid solution. The liquidus and solidus are so close together that there is little difference in composition between the portions which solidify first and those which solidify last, hence equilibrium is readily attained and the α solution is generally almost homogeneous in the chill-cast condition. The structure of these alloys undergoes exactly similar changes to those occurring in the zinc–copper α solid solution as a result of rolling and annealing, recrystallisation, crystal growth and the formation of twin crystals (Fig. 284).

With little more than 7·5 per cent. of aluminium the β constituent appears in alloys which have received a moderate rate of cooling, though the α solution can retain as much as 9 per cent. at atmospheric temperature. As usual, the β solution is harder and less ductile than α, and its presence strengthens the alloy. The alloys containing α may be rolled hot or cold (they are less fragile at the temperature of hot-rolling than the zinc–copper α alloys), but those containing $\alpha + \beta$ are only rolled hot. The 10 per cent. aluminium–copper alloy has the best mechanical properties of the series and is in use for purposes where strength combined with exceptional resistance to corrosion is required. Chill-castings of this alloy consist of about equal parts of α and β (Fig. 285). In rolled rod the constituents are banded in the direction of rolling (Figs. 286 and 287). Quenched from a high temperature it assumes great hardness, and consists almost entirely of β, showing an acicular structure similar to martensite (Fig. 289). To preserve the high quality of the alloy it is essential that the rate of cooling of the casting or hot-rolled rod should be such as to prevent the occurrence of the change $\beta \rightarrow \alpha + \delta$ at 560° C. When slowly cooled the β constituent is resolved into a duplex eutectoid structure; the presence of the δ constituent has an embrittling effect and ruins the properties of the alloy (Fig. 288).

Nickel–Copper Alloys

The principal nickel–copper alloys in commercial use are those containing the following percentages of nickel :—

2 to 3 per cent.	Substitute for copper for firebox stays.
15 to 20 ,, ,,	Condenser tubes: bullet envelopes.
25 ,, ,,	Coinage.
40 to 45 ,, ,,	Electrical resistances and thermo-couples, Constantan, Eureka, etc.

and also Monel metal (or the similar alloy Corronil), which contains 68 to 70 per cent. of nickel, about 28 per cent. of copper and appreciable amounts of iron and manganese, and is remarkable for its resistance to corrosion.

Since copper and nickel form a continuous series of solid solutions (Fig. 62), all these alloys in the annealed condition have a similar microstructure (Fig. 66). They are not subject to season cracking, but in all the nickel-rich alloys exposure to oxidising or sulphurising gases at the rolling temperature gives rise to intercrystalline cracking. Intercrystalline brittleness (shown in the microstructure by a thickening and darkening of the intercrystalline boundaries in the etched section) is developed in 80 : 20 cupro-nickel, but its origin may be different. This brittleness is usually considered to be associated with the precipitation of graphitic carbon, and on this account the percentage of carbon in cupro-nickel is kept as low as possible, usually below 0·04 per cent. The 80 : 20 type of alloy containing 1 per cent. of manganese and about 0·15 per cent. of silicon will undergo temper hardening with marked improvement in mechanical properties on reheating at 550° after quenching from 900° C.* The effect is due to the decreasing solubility of the compound Ni_2Si in cupro-nickel with fall of temperature. The saturated solid solution contains 0·6 per cent. of silicon at 900° C., 0·1 per cent. at 500° C. and probably less at atmospheric temperature. In the alloy

* D. G. Jones, L. B. Pfeil, and W. T. Griffiths, "Nickel–Copper Alloys of High Elastic Limit," *Journal of the Institute of Metals*, 1931, (2), vol. xlvi, p. 423.

containing 1 per cent. of manganese and 0·15 per cent. of silicon, hardened by the treatment described above, no precipitated particles are visible under the microscope, but visible precipitation of Ni_2Si occurs when the silicon content is higher.

The addition of aluminium to various copper–nickel alloys also gives rise to several important temper-hardening materials including " K " Monel which combines high tensile strength with good corrosion resistance.

Nickel–Zinc–Copper Alloys. Nickel Silvers

Nickel silvers are classified mainly on their nickel content. In all cases the microstructure should be that of a uniform solid solution, but as diffusion of nickel is slow, the macro-structure may show indications of the original dendritic structure, which is very pronounced in the cast alloy. The structure will also reveal the presence of lead in globules or films if this metal has been added to improve machinability; but lead should not be present in material which has to be spun or drawn, as it diminishes the ductility of the alloy.

Nickel silver is subject to season cracking under similar conditions to the brasses, and, like them, is rendered immune by low-temperature annealing.

Practical Notes

Macro-examination of Copper Alloys.—The preliminary examination of defective non-ferrous alloys should always include a macro-examination (Figs. 290 to 296).

In the examination of cast alloys for defects such as blow-holes, cavities, porosity and inclusions which arise from unsuitable casting conditions the macro-examination of as large an area as possible is essential. In addition, many defects in the wrought metal, such as blisters, spills and laminations, are traceable to imperfections in the ingot, and in the investigation of the causes of such defects a study of the macrostructure of ingots is of importance. Macro-examina-

tion is the most valuable means available for the examination of defective extruded alloys. A study of the macrostructure of billets at various stages of extrusion, and of the extruded rod produced from them, has revealed a large amount of information about the flow of metal in the extrusion process.

From small ingots and castings complete sections are prepared by sawing and, in the harder alloys, by grinding by an emery wheel with a copious supply of water or, in the very soft alloys, by shaping with a sharp tool. The sections are then rough-polished by the methods used for micro-sections, though the finish required is much less perfect than for micro-examination.

A longitudinal axial section of an ingot usually gives most information, but transverse sections below the head are useful if the ingot must not be destroyed. In castings cut up for special examination, sections through the risers and at heavy sections in the castings should be included. In alloys which have been worked the metal should be sectioned in such a way as to reveal deformation, flow structure, and grain size as completely as possible. In bar, rod and wire longitudinal axial sections are usually cut. Transverse sections will disclose cracks, seams and surface defects, and longitudinal tangential sections, formed by grinding flats on the surface, will reveal their extent.

Nitric acid (sp. gr. 1·2) may be used to reveal the structure of a machined or ground surface. A more carefully prepared surface may be etched for macroscopical examination by solutions of ammonia, ammonium persulphate or ferric chloride similar to, but stronger than, those used for micro-examination. The ferric chloride solution gives greater contrast between the different crystals and is useful for revealing the dendritic structure in α solid solutions. An ammoniacal solution of ammonium persulphate should preferably be used for brasses containing the β-phase. Good contrast, especially in alloys containing both α and β constituents, is also obtained by etching with an ammoniacal solution of copper ammonium chloride. This is prepared by adding

FIG. 290.—Longitudinal section of part of a strip ingot of 70 : 30 brass, showing columnar crystals penetrating to the centre towards the lower end, and similar crystals enclosing equiaxial crystals higher up in the ingot.

Etched with ammoniacal solution of ammonium persulphate. Actual size.

FIG. 291.—Axial section of the remains of a cast 6-inch diameter billet of 60 : 40 brass from which rod has been extruded by the inverted process.*

The structure reveals the direction of flow of the metal. The very coarse crystallisation at the end of the billet is due to grain growth following the slight deformation experienced in that region. In the forward part of the billet where deformation has been severe, recrystallisation has occurred.

Etched with 40 per cent. nitric acid.

About half actual size.

FIG. 292.—A similar axial section of an extruded rod and the remains of the billet from which it was being extruded by the inverted process.

Etched with 40 per cent. nitric acid.

About half actual size.

FIG. 293.—Transverse section of part of a strip ingot of 70 : 30 brass showing the wedge formation of columnar crystals which grow out at right angles to the surface of the mould and meet on intersecting planes inclined at 45 degrees to the surface.

Etched with ammoniacal solution of ammonium persulphate. Actual size.

* R. Genders, "The Extrusion of Brass Rod by the Inverted Process," *Journal of the Institute of Metals*, 1924, (2), vol. xxxii, p. 313.

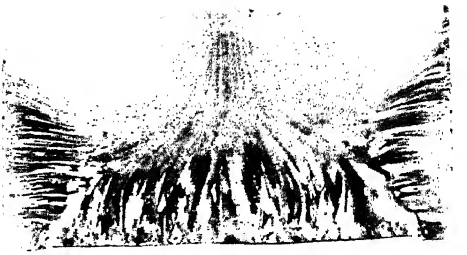

FIG. 291.

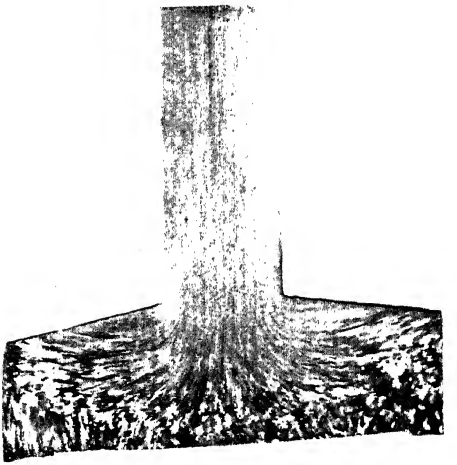

FIG. 292.

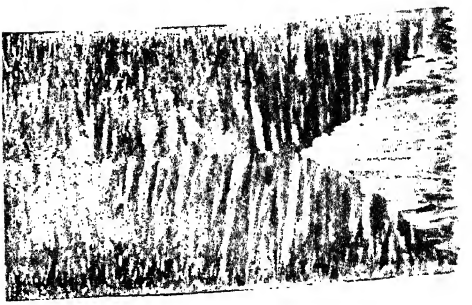

FIG. 293.

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PLATE LIV.

FIG. 294

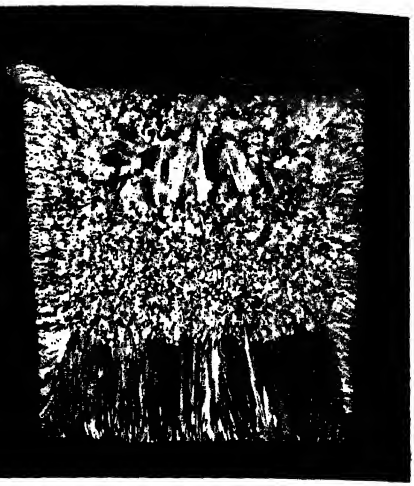


FIG. 295.

FIG. 296.

Macrostructure of copper alloys.

Repeatedly polished and etched with ferric chloride solution.

FIGS. 294 and 295.—Structure of ingots cast by the Durville rotatory method under identical conditions of temperature into a mould with pre-heated refractory sides and a water-cooled copper base, illustrating the restriction of crystal growth by certain alloying additions.

Two-thirds actual size.

FIG. 294.—Copper + 1 per cent. zinc.

FIG. 295.—Copper + 0·1 per cent. titanium.

Pure copper cast under these conditions is completely dendritic. The effect of zinc, aluminium and vanadium in restricting crystal growth is very small; on the other hand that of titanium, tin, oxygen, sulphur, selenium, tellurium, etc., is considerable.

L. Northcott: "The Influence of Alloying Elements on the Crystallisation of Copper," *Journal of the Institute of Metals*, 1938, (1), vol. lxii, p. 101.

FIG. 296.—Macrostructure of a 20 lb. ingot of 2 per cent. aluminium–copper alloy cast in a similar way to the above. × 3.

The base of the ingot was on the right of the photograph, the part shown uppermost being a side which was in contact with the hot refractory wall. The columnar crystals growing from the chilled base of the ingot were oriented so that one of the cube faces of the lattice was parallel to the direction of growth.

L. Northcott and D. E. Thomas: "Dendritic Structures," *Journal of the Institute of Metals*, 1939, (2), vol. lxv.

strong ammonia to a 10 per cent. solution of copper ammonium chloride until the precipitate first formed is redissolved. With any of these reagents the specimen may be partly immersed in the solution contained in a dish and the surface flooded by rocking the dish; or the surface may be swabbed with a soft cotton rag dipped in the reagent. The specimen is then washed first in water, then in acetone and dried. If it contains cavities it may be left immersed in acetone for 5 minutes or more to allow water to diffuse out, and it is desirable to give a final washing with ether to promote rapid drying. The surface may be preserved by applying a thin clear lacquer.

Test for internal stress.—The specimen (*e.g.* stamping, length of tube, rod, etc.) after being cleaned is immersed for 30 secs. in a mixture of 40 volumes of nitric acid (sp. gr. 1·42) and 60 volumes of water at room temperature, and is then thoroughly washed in running water. It is transferred while still wet to a solution containing 1 gram of mercurous nitrate crystals and 1 c.c. of nitric acid (sp. gr. 1·42) per 100 c.c. of distilled water, and allowed to remain for 5 minutes. On removal from the solution the brass is washed with water and acetone and allowed to dry untouched. Highly stressed brass will already show cracks, but if no cracks develop within 24 hours the brass may be regarded as free from internal stress likely to result in season cracking.

Micro-examination of Copper Alloys.—Small specimens selected from suitable positions are polished by the methods adopted for copper (p. 207) if the alloy is very soft, or for some of the harder duplex alloys a satisfactory finish is obtained with diamantine.

Specimens should be examined under the microscope before etching to detect oxides, inclusions, insoluble elements such as lead in brass. Any relief effects due to the presence of hard constituents will at the same time be observed. In some cases polish attack on a pad moistened with ammonia gives good results if practised with care.

Etching reagents suitable for almost all copper alloys are:

(1) A 10 per cent. aqueous solution of ammonium persulphate. This gives clear uniform etching of brass. The addition of 25 per cent. of 0·880 ammonia to the solution gives more rapid etching.

(2) An acid aqueous solution of ferric chloride. It is advisable to keep a stock solution containing:—

Ferric chloride . . .	10 grams.
Concentrated hydrochloric acid .	30 c.c.
Water	120 c.c.

and to dilute with water as may be required. To etch nickel-rich alloys, solution of the full strength is required; for copper-rich α solutions, 1 part of this solution to 2 parts of water gives satisfactory results. Heycock and Neville used a very dilute solution containing $3\frac{1}{4}$ grams of $FeCl_3$ and 25 c.c. HCl to 1000 c.c. water.

The multiplicity of special brasses and bronzes and their resistance to attack, especially that of the high-nickel alloys, have led to the use of other reagents, including the two types mentioned below.

A mixture of nitric and acetic acids is useful for etching pure nickel and alloys high in nickel. The solution contains:—

50 c.c. nitric acid (sp. gr. 1·42)
25 c.c. glacial acetic acid.
25 c.c. water.

Care is required in mixing the solution: the acetic acid should be added slowly, with constant stirring, to the diluted nitric acid.

Various chromic acid solutions give good results with complex brasses, bronzes and nickel alloys. They give a clean uniform etch, and if β is present the alloy may subsequently be etched in ferric chloride solution to give better contrast. Such solutions are: (1) saturated aqueous solution of CrO_3 or (2) 100 c.c. saturated solution $K_2Cr_2O_7$ + 10 c.c.

concentrated sulphuric acid (sp. gr. 1·84). To each of these solutions it is desirable to add 1 drop of concentrated hydrochloric acid per 25 c.c. at the time of use.

Heat tinting is useful for some bronzes, especially phosphor–bronzes.

Electrolytic etching may give valuable results, particularly in the case of severely cold-worked alloys and alloys rich in nickel.* As a general method of etching, however, it possesses no advantages over the use of ordinary reagents.

* For details see F. Adcock, "The Electrolytic Etching of Metals," *Journal of the Institute of Metals*, 1921, (2), vol. xxvi, p. 361.

CHAPTER XIV

THE STRUCTURE AND PROPERTIES OF ALLOYS OF ALUMINIUM AND OF MAGNESIUM

SOME reference has already been made to the difficulties encountered in the preparation of aluminium and its alloys for microscopical examination. These difficulties retarded progress in the metallography of aluminium alloys in the early days of their development, but now, both as regards technique in microscopical examination and the completeness of the interpretation of their constitution, the aluminium alloys occupy a foremost place among the non-ferrous metallic materials.

Though aluminium of a high degree of purity (99·995 per cent.) can be produced, commercial aluminium usually contains about 99 per cent. of aluminium, the chief impurities being silicon and iron. The iron usually occurs as a compound $FeAl_3$, which is almost insoluble in aluminium, with which it forms a eutectic containing about 2 per cent. of iron. The silicon is partly in solid solution, but may also be visible under the microscope as crystals of free silicon, or as a complex constituent containing aluminium, silicon and iron, two such constituents having been identified in specimens of commercial aluminium. Cast aluminium (unless very pure—Fig. 301) shows a dendritic structure, the less pure portion which solidifies last being forced to the grain boundaries. The rolled and annealed metal shows equiaxial grains in which particles of $FeAl_3$ and the complex silicon solid solution (often referred to as X) are embedded.

Though valuable on account of its resistance to corrosion and electrical properties, aluminium finds most of its practical applications in the form of its alloys, which exhibit greater

strength than the pure metal while retaining the advantages of low specific gravity.

All the commercially important aluminium alloys on solidification form dendritic crystals of aluminium-rich solid solutions. The material of lower melting point is entrapped between the primary crystals, the dendritic character of which may not be very apparent when the alloy consists of 95 per cent. or more of aluminium. This lack of uniformity of composition is eliminated in the wrought alloys, many of which consist of a single solid solution (with insoluble impurities such as $FeAl_3$) at the temperatures at which they are worked. Most of the aluminium solid solutions which are stable at high temperatures may by quenching be preserved in the supersaturated condition at atmospheric temperature, and subsequent ageing or tempering induces breakdown of the supersaturated solid solution, accompanied by increase in hardness.

Cast Alloys of Aluminium

Copper–Aluminium Alloys.—The copper–aluminium alloys show a eutectic at 32 per cent. copper. Aluminium will retain as much as 5 per cent. of copper in solid solution at 500° C., but only 0·5 per cent. at ordinary temperatures (diagram, Fig. 297); but, on account of the large interval between liquidus and solidus and the fact that at temperatures just below the melting point diffusion is slow, equilibrium is very rarely attained. The result is that alloys with only 2 per cent. of copper frequently show the $CuAl_2$–aluminium eutectic. With higher copper content, such as the 8 or 12 per cent. alloys employed commercially, the cast alloys show a well-marked dendritic structure.

The copper–aluminium alloys are generally used in the cast condition, and those containing between 2 and 5 per cent. of copper may be improved by heat treatment consisting of quenching from 500° C., followed by ageing at atmospheric temperature or by heating at a temperature

not exceeding 200° C. By this means precipitation of $CuAl_2$ is effected in particles which may be too fine to be recognised microscopically, while the tensile strength is raised from 12 to over 20 tons per square inch, and the elongation, though reduced, remains at a high figure. Ageing at atmospheric temperature is slow, and the process is frequently hastened by heating at 120° to 150° C. for 1 or 2 days. A higher temperature which brings about coalescence of the $CuAl_2$

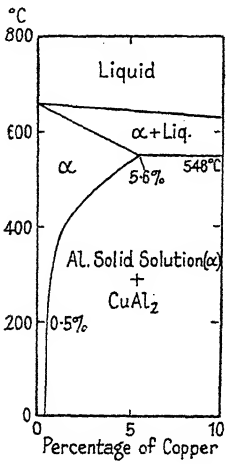


FIG. 297.—Constitutional Diagram indicating Solid Solubility of Copper in Aluminium. (*Stockdale; Dix and Richardson.*)

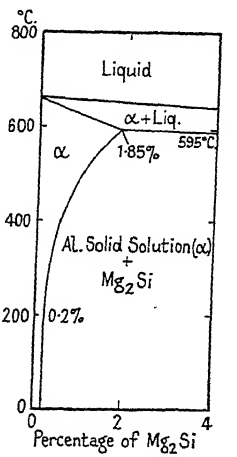


FIG. 298.—Constitutional Diagram indicating Solid Solubility of Magnesium Silicide in Aluminium (*Dix, Keller, and Graham.*)

into visible particles is less efficient. The copper–aluminium alloys intended for heat treatment frequently contain silicon in amounts up to 3 per cent.

Silicon–Aluminium Alloys.—The silicon–aluminium alloys show a eutectic containing 11·6 per cent. of silicon (Fig. 299), but alloys containing as much as 14 per cent. of silicon can be made to solidify without separation of primary silicon. This effect can be produced either by rapid cooling, as in chill-castings of small dimensions, or by certain agents known as "modifiers," of which the most important is sodium, only a trace of which should enter the metal. The effect is prob-

ably due to under-cooling, which results in an apparent shift of the eutectic composition to a higher silicon content. The most important feature of the modification process is the

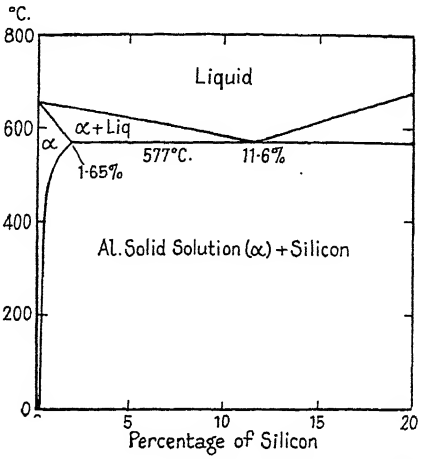


FIG. 299.—Constitutional Diagram of Silicon–Aluminium Alloys (*Dix and Heath*).

refinement of the structure of the silicon–aluminium eutectic, brought about by the rapid formation of nuclei resulting

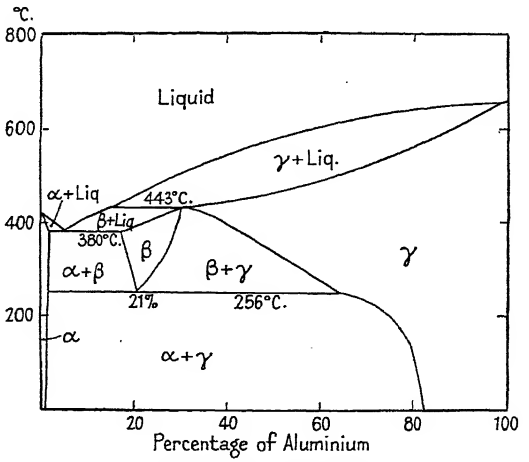


FIG. 300.—Constitutional Diagram of the Aluminium–Zinc Alloys.*
(*Hanson and Gayler, Peirce.*)

* This diagram is undergoing considerable revision especially in the central region, 20 to 80 per cent. of aluminium, but the necessary modifications are still under discussion. The true solid solubility of zinc in aluminium at 100° C. is now given as only about 5 per cent.

from under-cooling or the action of the modifying agent or both (Figs. 305 to 308).

A marked improvement in mechanical properties accompanies the change of structure produced by modification which is applied commercially to alloys containing 10 to 13 per cent. of silicon. Their tensile strength is raised from 8 to about 13 tons per square inch and elongation from 5 to over 15 per cent.

Zinc–Aluminium Alloys.—With up to 18 per cent. of zinc at atmospheric temperature, or up to 40 per cent. at 300° C., these alloys consist of a single solid solution (Fig. 300), and the rolled and annealed 15 per cent. zinc alloy presents a uniform appearance of polygonal grains (Fig. 310). The chill-cast metal, however, shows pronounced coring (Fig. 309). There is little commercial use for the binary zinc–aluminium alloys which become brittle when 15 per cent. of zinc is exceeded. The best known of the ternary alloys is that containing 12 per cent. of zinc and 3 per cent. of copper, which shows $CuAl_2$ embedded in the zinc–aluminium solid solution.

Wrought Alloys of Aluminium

The wrought alloys of aluminium are dependent for their good mechanical properties on the effect of cold-work, or of heat treatment, or on the combined action of the two produced by cold-working the quenched alloy which is subsequently allowed to age-harden.

Copper–Aluminium Alloys.—In the wrought alloys copper is rarely allowed to exceed 4·5 per cent. They may contain in addition up to 2 per cent. of silicon and possibly 1 per cent. of manganese. The 5 per cent. copper–aluminium solid solution is capable of dissolving 1·5 per cent. of silicon at the eutectic temperature. Manganese will also pass into solid solution. The mechanical properties of these alloys are improved by a heat treatment similar to that applied to the cast alloys of copper and aluminium.

Magnification 100 diameters.

FIG. 301.—Pure cast aluminium (over 99·7 per cent.) containing iron 0·06 per cent., silicon 0·16 per cent.

Etched with 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water.

FIG. 302.—Copper–aluminium alloy die-casting (copper 8 per cent.) showing small grains of aluminium surrounded by the aluminium–$CuAl_2$ eutectic (dark).

Etched with 10 per cent. sodium hydroxide in water.

FIG. 303.—Copper–nickel–aluminium alloy, as cast (copper 4·1 per cent., nickel 2·2 per cent.), showing aluminium with a eutectic structure formed by aluminium, $CuAl_2$ and $NiAl_3$.

Polished in relief with neutralised "Silvo" metal polish.

Unetched.

FIG. 304.—Nickel–aluminium alloy, as cast (nickel 4·3 per cent.), showing aluminium and the aluminium–$NiAl_3$ eutectic. The feathery appearance is characteristic of this eutectic. The dark needles are probably $FeAl_3$.

Etched with 1 per cent. hydrofluoric acid and 50 per cent. nitric acid in water.

FIG. 305.—Silicon–aluminium alloy, large sand-casting (silicon 10·8 per cent.). White dendritic crystals of aluminium embedded in dark groundmass of the aluminium–silicon eutectic, the fine granular appearance of which indicates "modification" of the alloy.

Etched with 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water.

FIG. 306.—Silicon–aluminium alloy die-casting (silicon 13 per cent.). Modified structure.

Small grains of aluminium (light) embedded in aluminium–silicon eutectic (dark) which shows a fine granular structure. The dark needles are the iron–aluminium compound $FeAl_3$.

Etched with 20 per cent. sulphuric acid at 70° C.

FIG. 301.

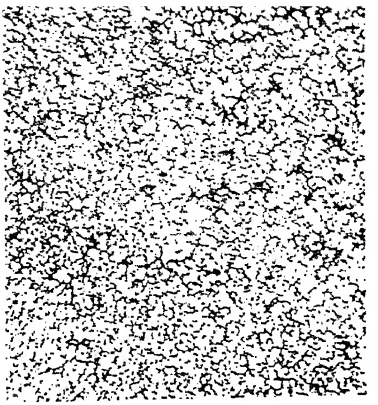


FIG. 302.

FIG. 303.

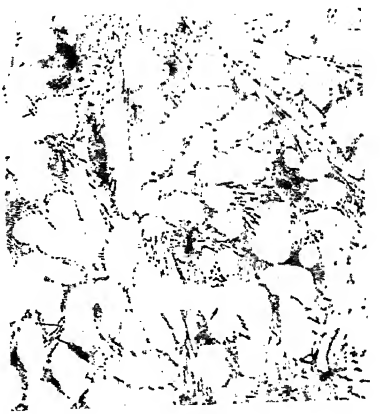


FIG. 304.

FIG. 305.

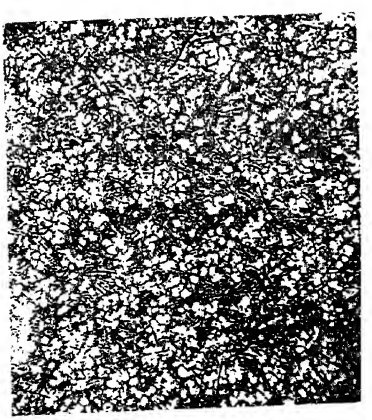


FIG. 306.

[Facing p. 244.

PLATE LVI.

FIG. 307.

FIG. 308.

FIG. 309.

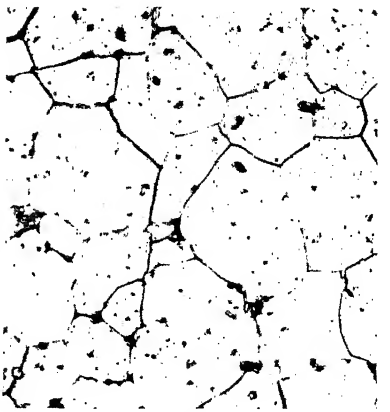


FIG. 310.

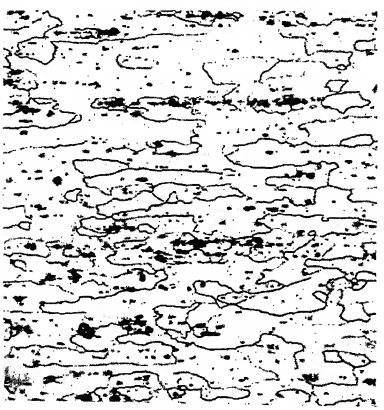


FIG. 307.—Silicon–aluminium alloy chill-casting (silicon 11·0 per cent., iron 1·3 per cent.). Unmodified structure.

The centre of the casting showed the unmodified structure consisting of aluminium in which the silicon has separated in the form of relatively large plates and needles.

Unetched. × 500.

FIG. 308.—The same alloy. Modified structure.

The edges of the chill-casting showed the modified structure consisting of dendritic grains of aluminium (light) set in a fine granular eutectic of aluminium and silicon. The iron content of this alloy is high, a feature which is likely to cause brittleness. The iron occurs in two forms, dark needles of $FeAl_3$, fairly uniformly distributed, and occasional grey plates of a silicon-rich iron–aluminium–silicon constituent. One of these inclusions is shown in the field selected. The typical structure, however, is represented by the lower part of the photomicrograph.

Etched with 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water. × 500.

FIG. 309.—Cast zinc–aluminium alloy containing 20 per cent. of zinc, showing dendrites of the γ-solid solution relatively poor in zinc surrounded by γ solution richer in zinc, in which the impurities and grain boundaries occur.

Etched with 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water. × 100.

FIG. 310.—Hot-rolled commercial zinc–aluminium alloy, containing 15 per cent. of zinc and showing polyhedral grains of solid solution with impurities, chiefly $FeAl_3$ (black) in the form of globules.

Etched with 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water. × 100.

FIG. 311.—Hot-rolled Duralumin sheet (20 S.W.G.) to B.S.S. 5L3 (approximate composition: copper, 4·0, manganese 0·6, iron 0·5, magnesium 0·5, silicon 0·3 per cent.).

The groundmass is a solid solution, the small dark particles are probably $FeAl_3$ or a complex constituent containing iron, and the larger particles undissolved $CuAl_2$ or $MnAl_3$.

Etched with 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water. × 100.

FIG. 312.—Sand-cast magnesium alloy ("elektron" containing aluminium 4, zinc 3, manganese and copper, each about 0·3, and magnesium 92 per cent.).

Polyhedral crystals of solid solution showing coring, and some undissolved constituents (possibly MgZn or Mg_2Cu) at the grain boundaries.

Etched with 2 per cent. nitric acid in alcohol. × 100.

Complex Alloys containing Magnesium and Silicon.—The most widely used wrought alloys containing copper are those containing magnesium and silicon as well as manganese or nickel, the two most important types being Duralumin and "Y"-alloy. The improvement produced by heat treatment in both these alloys depends to some degree on the presence of magnesium silicide.

Duralumin contains approximately 4 per cent. of copper and 0·5 per cent. each of manganese, magnesium and silicon. If quenched from 470° to 490° C. the alloy is softened, but it progressively hardens on keeping at atmospheric temperature. The age-hardening is almost complete in 4 days. If the alloy age-hardened at room temperature is reheated for 20 hours at temperatures up to 125° C. some softening occurs, but after heating at higher temperatures, for example, 150° to 175° C. (or still higher for shorter times), maximum hardness is attained. The hardening is due to the possibility of precipitation of both $CuAl_2$ and Mg_2Si from solid solution (Figs. 297, 298); there is, however, no change in the microstructure on ageing. In the simplest terms it may be considered that the hardening at room temperature is due to precipitation of ultra-microscopic particles of Mg_2Si and the further hardening at raised temperatures to a similar precipitation of $CuAl_2$; but precipitation even on an ultra-microscopic scale is preceded by the formation of nuclei as a result of the diffusion of atoms to the planes at which precipitation will subsequently occur and this nucleus-formation is in itself sufficient to cause lattice distortion and hardening.*

In the more recently developed alloy, Super-Duralumin, the copper is increased to 4·5 per cent. and the silicon to 1·2 per cent. To bring out the best properties of this alloy a tempering or "artificial ageing" treatment at 175° C. is essential.

Under certain conditions of use (as, for example, exposure

* M. L. V. Gayler, "The Theory of Age Hardening," *Journal of the Institute of Metals*, 1937, (1), vol. lx, p. 249; and "Ageing," *The Metallurgist*, 1938, vol. xi, pp. 166 and 181.

to sea-water), Duralumin and some alloys of similar composition develop a serious type of intercrystalline corrosion, visible under the microscope as intercrystalline cracking, with few external signs of corrosive attack.* The defect is analogous, on the one hand, to season cracking of brass because it is accelerated, even if not initiated, by stress in the metal, and on the other hand to weld decay in austenitic nickel–chromium steels because it has been proved that conditions at the crystal boundaries are very important. A relatively high quenching temperature and a rapid rate of cooling through the range of temperature in which precipitation of $CuAl_2$ and of Mg_2Si would occur freely on slow cooling are found to confer increased resistance to intercrystalline corrosion.

"Y"-alloy differs from Duralumin in containing more magnesium (1·5 per cent.) and 2 per cent. of nickel instead of manganese. Its heat treatment is similar to that of Duralumin, and consists of heating at 510° to 520° C. for $\frac{3}{4}$ hour, quenching in boiling water and allowing to age for 5 days. The hardening is associated with the precipitation of Mg_2Si and of the copper–nickel–aluminium constituent which replaces $CuAl_2$. The properties of "Y"-alloy are similar to those of Duralumin at atmospheric temperature, but are superior at raised temperatures. Unlike Duralumin, it has excellent properties in the condition as cast and heat-treated (quenched and aged). Castings require a longer preliminary heating (about 6 hours at 530° C.) before quenching, than the wrought alloy.

Magnesium–Aluminium Alloys.—Alloys containing up to 1 per cent. magnesium with 0·5 to 2·0 per cent. of silicon have been found useful for difficult stampings, on account of their softness at high temperatures. They may also be cold-stamped in the quenched condition, and subsequently acquire very good properties by precipitation of Mg_2Si on ageing.

* A. J. Sidery, K. J. Lewis and H. Sutton, "Intercrystalline Corrosion of Duralumin," *Journal of the Institute of Metals*, 1932, (1), vol. xlviii, p. 165; K. L. Meissner, "The Effect of Artificial Ageing upon the Resistance of Super-Duralumin to Corrosion by Sea Water," *ibid.*, 1931, (1), vol. xlv, p. 187.

When the magnesium content reaches 5 per cent. no age-hardening takes place after quenching, even when silicon is present, and alloys with more than this amount depend on cold-working for any variation in mechanical properties that they can undergo. The tensile strength of alloys containing 7 or 8 per cent. of magnesium can in this way be varied from 20 to 30 tons per square inch, with a corresponding fall in elongation from 20 to 5 per cent. Such alloys (often containing a little manganese) have a good resistance to atmospheric corrosion and to attack by sea-water.

Magnesium Alloys

Magnesium of high purity can be obtained commercially, but its use is limited by the fact that it is weak, soft and inferior to aluminium in ductility and elastic properties. When alloyed with small quantities of other metals, notably aluminium or zinc, it provides a series of alloys of specific gravity, 1·75 to 1·9, having a wide range of properties. Almost all the alloys of practical importance consist of solid solutions of the added metal in magnesium. Magnesium forms hard and brittle compounds with most of the metals in common use, and the presence of a second constituent in the microstructure, even as a eutectic, has a deleterious effect on ductility.

The most important types of magnesium alloys are those containing (*a*) 4 to 10 per cent. of aluminium with about 0·4 per cent. of maganese; (*b*) 4·5 per cent. of zinc with about 0·5 per cent. of copper or manganese; and (*c*) 3 to 10 per cent. of copper. As copper is almost insoluble in magnesium, and forms a eutectic containing Mg_2Cu, the copper–magnesium alloys are only suitable for hot-working when the copper content is low (3 per cent.) and when the improvement in properties is consequently slight. The applications of copper–magnesium alloys have therefore been few and mainly confined to their use as castings. In the presence of aluminium

or of zinc, copper passes into solid solution, and it may therefore with advantage be employed in the first and second groups of alloys mentioned above. In the first group some of the aluminium may be replaced by 1 to 3 per cent. of zinc (Fig. 312). These aluminium–magnesium alloys are by far the most important group, both as regards mechanical properties and resistance to corrosion.

Except in a marine atmosphere, the corrosion resistance of many magnesium alloys is satisfactory, and it has been further improved by the application of suitable methods of protection, such as anodic oxidation, varnishing, enamelling and coating with other metals.

Practical Notes

Aluminium and its Alloys

Macro-examination.—The section should be machined to give a smooth surface and ground on coarse and fine emery papers which may, if desired, be mounted on power-driven discs and should be soaked in paraffin. Sand-cast specimens of large grain size do not need such careful preparation as those showing a finer structure.

The surface must be freed from grease by cleaning with benzene or carbon tetrachloride and the specimen, previously warmed by immersion in hot water, may then be etched by swabbing with a 20 per cent. aqueous solution of hydrofluoric acid. When etching is complete the specimen is washed in water, then in acetone, and dried.

A more vigorous attack, obtained without warming the specimen, is produced by the following solution (C. M. Tucker):—

45 c.c. hydrochloric acid (sp. gr. 1·18)
15 c.c. hydrofluoric acid (sp. gr. 1·15)
15 c.c. nitric acid (sp. gr. 1·42)
25 c.c. water.

Hume-Rothery's reagent, developed for use with silicon-aluminium alloys but suitable also for other aluminium alloys, consists of an aqueous solution of cupric chloride containing 150 grams per litre. The specimen is immersed for 5 to 10 seconds, removed from the solution, and the surface freed from copper by brushing under water. The specimen is then re-immersed and the process repeated until the desired depth of etching is produced. If copper adheres strongly to the surface it can be removed by dipping the specimen in 50 per cent. nitric acid. A considerable brightening of the appearance can be obtained after the final treatment with cupric chloride by dipping the alloy into this solution or into a saturated solution of chromic acid in water.

Ink prints, made in the same way as from steel specimens, may be used to record all cavities, except very fine pinholes and cracks, present in etched sections from castings (Hanson), but cannot be used to reproduce the structure.

Polishing.—The finer emery papers employed should be sheets which, though not actually worn out, have had some use, so that the loose and coarser particles have been removed. They should be waxed by the application of a strong solution of white wax in benzene which is allowed to dry off; or they may merely be soaked in paraffin.

Rubbing of the specimen on all grades of emery should be gentle and light. After leaving the last emery paper (an old piece of 00), the surface of the specimen should appear clear and bright, with no suggestion of a dark patina or film.

Polishing, or removal of fine emery scratches, may be most quickly effected on a rotating pad impregnated with one of the commercial liquid metal polishes; relief polish is obtained, accompanied by some chemical attack, so that micro-constituents are visible under the microscope; but the appearance varies with polishing conditions, such as speed, pressure, and time taken, and may be deceptive.

This relief polishing may be regarded as a means of quickly removing scratches, to be followed by a final polish on a pad

on the rotating wheel impregnated with a mixture of equal parts of powdered ammonium alum and heavy magnesia. The ammonium alum tends to prevent the formation of a patina on the specimen. A fairly high speed should be used, with a plentiful supply of water. A smooth surface, free from relief polish or chemical attack, should be obtainable in a comparatively short time. The precautions mentioned on page 9 should be observed in the use of magnesia.

An alternative method of polishing aluminium has frequently been used with success. The specimen is prepared in the usual manner, first on waxed emery papers and then on a polishing block fed with magnesia and water. A small piece of selvyt cloth is stretched on a board and soaked in benzene. A little alumina (very carefully prepared from pure recrystallised ammonium alum as described on page 9, and washed in water) is sprinkled on the cloth, with a few drops of distilled water. The polishing is continued by hand, a little more water being added from time to time if required. Within a few minutes a good surface, free from scratches and from any marked degree of relief or chemical attack, is obtained.

Etching.—The most useful reagent is probably a solution of 2 per cent. hydrofluoric acid and 25 per cent. nitric acid in water. The time of etching required is 30 seconds to 1 minute.

Aqueous solutions of hydrofluoric acid may be used alone in strengths varying from 1 to 10 per cent., adjusted to obtain maximum contrast in the appearance of different constituents of the alloy. Solutions containing 5 to 20 per cent. of potassium or sodium hydroxide in water are often employed, the stronger solutions for commercial aluminium and the weaker for alloys. The tarnish produced by hydrofluoric acid or the black deposit frequently formed on alloys etched in alkaline solutions, is removed by dipping the specimen in a saturated solution of chromic acid in water or in 50 per cent. nitric acid.

Magnesium and its Alloys

Polishing.—The initial preparation is similar to that of aluminium, the papers if necessary being flooded with paraffin to reduce friction. Except for the harder magnesium alloys, polishing on a rotating pad is too severe a treatment. Final polishing should be done by hand, with liquid metal polish on selvyt stretched on a board. A film of grease remains on the specimen, and is removed by gently rubbing the surface on selvyt wetted with benzene or acetone.

Etching.—A 1 or 2 per cent. solution of nitric acid in alcohol; or alcoholic acid ferric chloride solution consisting of 5 c.c. of the stock acid ferric chloride solution (p. 237) and 100 c.c. alcohol.

CHAPTER XV

THE STRUCTURE AND PROPERTIES OF ALLOYS OF ZINC, TIN, LEAD, AND OF BEARING METALS

Zinc and its Alloys

CERTAIN discontinuities in the physical and mechanical properties of zinc have led to the supposition that allotropic forms of the metal can exist. X-ray analysis of zinc crystals at different temperatures between 20° and 400° C. has, however, failed to reveal any change in the type of crystal structure, and it must accordingly be concluded that the changes observed are not due to the existence of true allotropic modifications of zinc.

Cast zinc shows large polyhedral grains. The chief impurities in commercial zinc are lead which collects in globules or is present in the grain boundaries, and iron which forms the compound $FeZn_7$, soluble in zinc to the extent of 0·02 per cent. at 418° C. and 0·008 per cent. at 20° C.

Tin–Zinc Alloys show a eutectic containing 92 per cent. of tin and melting at 199° C.; the solid solubility of tin in zinc is very small. Alloys with less than 92 per cent. of tin consist of zinc and eutectic. Very small amounts of tin are sufficient to give a complete film of zinc–tin eutectic around the zinc grains, causing brittleness at raised temperatures on account of the low melting point of the intergranular film.

Aluminium–Zinc Alloys.—Aluminium is soluble in zinc to the extent of 0·8 per cent. at 380° C., diminishing to 0·05 per cent. at atmospheric temperature. The solidification of alloys containing 5 to 15 per cent. of aluminium begins with the separation of the β solid solution and is completed by the formation of the $\alpha + \beta$ eutectic. The β present under-

goes a further transformation in the solid state, forming the eutectoid $\alpha + \gamma$ (Fig. 300).

An alloy containing 10 per cent. of aluminium consists of dendrites of β embedded in a groundmass of eutectic, but the β itself is broken down to $\alpha + \gamma$ (Figs. 315, 316), so that at atmospheric temperature the only constituents are the α and γ solid solutions.

The 6 per cent. alloy has a similar structure with a smaller proportion of the primary β constituent (Fig. 314). Alloys containing 3 per cent. of copper and 6 to 15 per cent. of aluminium show considerable strength in the cast condition (Fig. 313), but are unsuited for use as rolled bars or forgings since, in this condition, they deteriorate with time. Die-castings of these alloys are liable to develop cracks, as a result of intercrystalline corrosion. This cause of instability has now been overcome in certain compositions by the use of the highest grade of zinc in the manufacture of the alloys and the addition of a small amount of magnesium, not exceeding 0·08 per cent. The chief types are those containing about 4 per cent. of aluminium, or 4 per cent. of aluminium with 2 per cent. of copper. Although the alloy with copper is slightly stronger, the aluminium–zinc alloy without copper is more permanent in dimensions and impact value. The separate effect of the additions on the structure of zinc is shown in Figs. 327 and 328. Pressure die-castings of the alloys have a very fine structure, partly on account of rapid cooling and partly owing to the grain refinement produced by the addition of magnesium.

Tin and its Alloys

Commercial tin is usually of high purity. If melted at a low temperature and poured into an open stone mould it presents a brilliant white surface which, when etched, reveals the coarse crystalline structure of the metal. The presence of a little lead, iron or other impurity imparts a dull and frosted appearance to the surface. Microscopical examina-

tion is, however, of no value in detecting the impurities in tin, as they are usually present in very small amounts and many of them are in solid solution. A bar of pure tin when bent emits a characteristic sound called the "cry" of tin, due to breakdown of the structure with the formation of twin crystals.

When tin is exposed to severe cold, it disintegrates into a granular grey powder (grey tin). The disintegration does not readily take place, the maximum rate of change occurring at about $-50°$ C., but when once started, it may proceed at higher temperatures, especially in contact with certain solutions (*e.g.* tin ammonium sulphate) which will dissolve tin. The change may be of importance in connection with the storage of tin and tin articles in regions where the temperature can be very low. Reversion to the ordinary variety (white tin) does not occur below 16° C. Grey and white tin are definite allotropic modifications shown by X-ray crystal analysis to have different lattice structures.

Tin is extensively employed to coat mild steel in the manufacture of tin plate. Its resistance to corrosion even at temperatures up to 100° C. renders it a valuable metal for coating culinary vessels. The tin coating on tin plate is exceedingly thin (from 1 to 4×10^{-4} inch), and the chief application of microscopy in connection with tin plate (apart from the examination of the underlying metal) is in the study of the surface. Minute pores in the tin coating constitute centres at which corrosion of the underlying metal can begin and from which it will spread, and a macroscopic test to detect porosity has useful applications.* The extent and situation of the defects having been established, further microscopical investigation, including examination of the underlying metal at the site of the defect, may assist in determining the cause of the porosity.

* Two such tests are described and compared in a paper on "The Determination of the Porosity of Tin Coatings on Steel," by D. J. Macnaughtan, S. G. Clarke, and J. C. Prytherch, *Journal of the Iron and Steel Institute*, 1932, (1), vol. cxxv, p. 159.

FIG. 313.—Copper–aluminium–zinc alloy containing zinc 88·8 per cent., aluminium 7·8 per cent., and copper 3 per cent., showing grains of zinc-rich solid solution, and eutectic.
Etched with 1 per cent. nitric acid in alcohol.
× 100.

FIG. 314.—Aluminium–zinc alloy containing 6 per cent. of aluminium as cast, showing dendrites of β in a groundmass of the eutectic of the α and β solid solutions. After solidification the β constituent has partially broken down into the eutectoid $\alpha + \gamma$.
Etched with 5 per cent. nitric acid in alcohol.
× 100.

FIG. 315.—Aluminium–zinc alloy containing 10 per cent. of aluminium, as cast, showing dendrites of β (light) in a groundmass of the eutectic of the α and β solid solutions. The proportion of β which has separated is greater than in Fig. 314. After solidification, the β constituent has partially broken down to $\alpha + \gamma$, giving a mottled appearance to the primary dendrites.
Etched with 5 per cent. nitric acid in alcohol.
× 100.

FIG. 316.—The same alloy as shown in Fig. 315. β dark.
Etched with 10 per cent. sodium hydroxide in water. × 100.

Figs. 315 and 316 show the reversal of the etching effect on changing from an acid to an alkaline etching reagent.

FIG. 317.—Tin–lead alloy containing 50 per cent. of lead and 50 per cent. of tin (common solder), consisting of dendrites of lead in a groundmass of tin–lead eutectic.
Etched with nitric acid in alcohol. × 250.

FIG. 318.—Antimony–lead alloy containing 2 per cent. of antimony, as cast. The structure consists of crystals of lead containing antimony in solid solution partly surrounded by lead–antimony eutectic. Lead will retain about 2·45 per cent. of antimony in solid solution at the eutectic temperature and 0·25 per cent. at atmospheric temperature. The alloy heated to 240° C. and quenched shows age-hardening.
Etched with acetic acid and hydrogen peroxide.
× 50.

PLATE LVII.

FIG. 313.

FIG. 314.

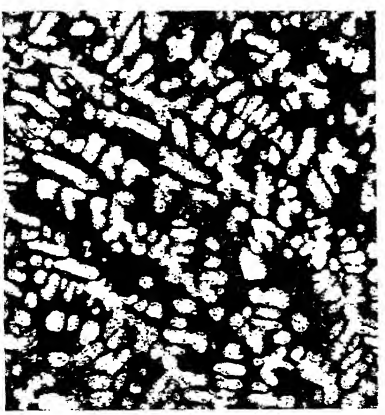


FIG. 315.

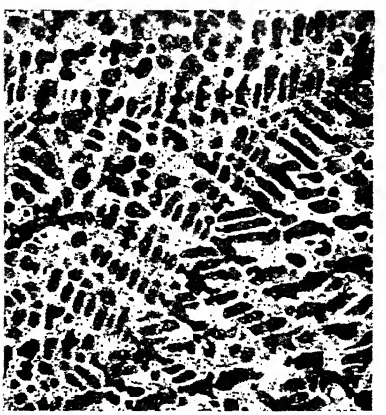


FIG. 316.

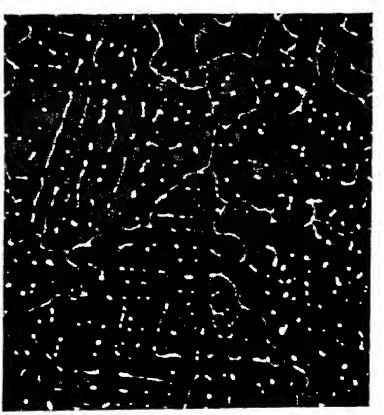


FIG. 318.

PLATE LVIII.

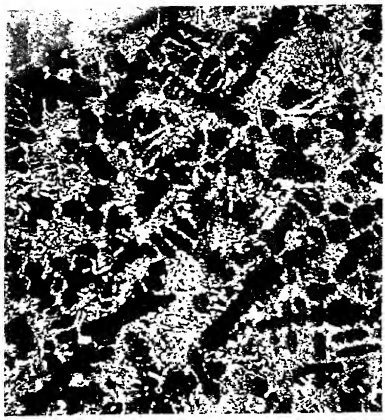


FIG. 319.

FIG. 320.

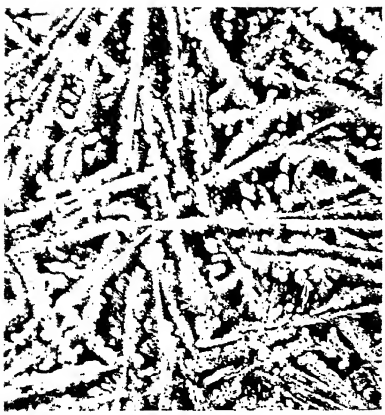


FIG. 321.

FIG. 322.

FIG. 319.—Antimony–lead alloy containing 9·0 per cent. of antimony, as cast. Dendritic crystals of lead (holding some antimony in solid solution) embedded in the lead–antimony eutectic. The eutectic contains 12·5 per cent. of antimony.

Etched with acetic acid and hydrogen peroxide.

× 250.

FIG. 320.—Calcium–lead alloy containing 1·5 per cent. of calcium, as cast. Crystals of Pb_2Ca are first formed, the remaining liquid solidifying as almost pure lead containing about 0·1 per cent. of calcium in solution.

The compound Pb_3Ca is hard and brittle and not appreciably affected by exposure to the air.

Etched with acetic acid and hydrogen peroxide.

× 100.

FIG. 321.—Copper–tin alloy containing 10 per cent. of copper. Hard needle-shaped crystallites of η solid solution (CuSn) in a groundmass of the copper–tin eutectic containing 1 per cent. of copper.

Etched with 5 per cent. solution of hydrochloric acid in water. × 25.

FIG. 322.—Copper–antimony–tin bearing metal containing 3·5 per cent. copper, 8·5 per cent. antimony, and the remainder tin. Cubic crystals and star-like crystallites approximating in composition to SbSn and CuSn respectively, set in a groundmass of tin containing antimony in solid solution, and forming a eutectic with some of the copper.

Etched with 5 per cent. hydrochloric acid in water. × 50.

FIG. 323.—Copper–antimony–tin bearing metal containing 1·5 per cent. of copper, 10 per cent. of antimony and the remainder tin. Similar in structure to the alloy shown in Fig. 322, but SbSn greater in amount, and CuSn much less in amount.

Etched with 5 per cent. hydrochloric acid.

× 25.

FIG. 324.—Tin–antimony–lead bearing metal containing tin 6 per cent., antimony 16 per cent. and the remainder lead. Cubic crystals (approximately SbSn) and grains of lead (dark) set in a groundmass of tin–lead–antimony eutectic.

Etched with 5 per cent. nitric acid in alcohol.

× 100.

Tin forms useful alloys with many metals, *e.g.* copper, lead, zinc and antimony. Of these the alloys with copper have already been dealt with.

Lead–Tin Alloys.—Tin and lead form a series of alloys which shows a eutectic containing 38 per cent. of lead and melting at 183°. C. (Fig. 325). Tin retains very little lead in solid solution at room temperatures, and the groundmass

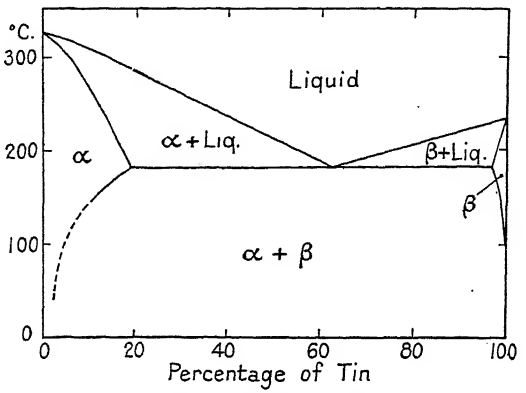


FIG. 325.—Constitutional Diagram of the Lead–Tin Alloys. (*Rosenhain and Tucker, Stockdale.*)

At 183° C. the solid solubility of tin in lead is 19·5 per cent. and of lead in tin 2·6 per cent.

of the tin-rich alloys consists of almost pure tin. The principal lead–tin alloys of industrial importance are :—

1. Pewter, containing upwards of 85 per cent. of tin, and thus consisting of tin and eutectic. There is a danger of lead-poisoning in the use of pewter vessels containing more than 18 per cent. of lead, *i.e.* more than 50 per cent. eutectic. Unalloyed tin is sometimes used in place of pewter. It is whiter in colour, and absence of lead renders it quite safe for domestic purposes. Antimony–tin alloys have also replaced pewter.

2. Solders. Tinman's solder, containing about 2 parts of tin and 1 part of lead, approximates to the eutectic composition. Common solder contains equal parts of the two metals (Fig. 317). Plumber's solder, containing about 2 parts of lead and 1 part of tin, has a range of solidification from 252° C.,

where lead first begins to separate, to 183° C., the freezing point of the eutectic. During this range of temperature in which lead is separating out, the alloy is in a pasty state, and this condition is utilised by the plumber for "wiping the joint."

The primary crystals in alloys, containing more than 38 per cent. of lead, and the lead-rich constituent of the eutectic are not pure lead, but contain tin in solid solution. Lead dissolves 19·5 per cent. of tin at 183° C. below which temperature the tin content of the saturated solid solution diminishes to about 2 per cent. at 25° C.

Antimony–Tin Alloys.—The binary alloys are not usually employed, but form the basis of more complex alloys, such as Britannia metal and the bearing metals.

Britannia metal is a ternary alloy of antimony, copper and tin having a range of different compositions. English Britannia metal contains 90 to 94 per cent. of tin with 4·5 to 9 per cent. of antimony and 1·5 to 0·5 per cent. of copper, the high-antimony low-copper variety being used for castings. In the cheaper alloys (used for castings only) zinc replaces some of the tin. The properties may be considerably affected by heat treatment, such as quenching from 200° C. and ageing.

In the absence of copper the structure consists of the δ solid solution of antimony in tin. The binary alloys of antimony and tin form a series of four solid solutions, that richest in antimony being usually referred to as α and that richest in tin as δ. If the antimony exceeds about 9 per cent., cubic crystals of the γ constituent (which may be seen in Fig. 324) are present. The modification in structure introduced by the presence of copper is not definitely known. Britannia metal in the cast condition shows small bright-etching needles or globules (possibly the copper–tin η solution) embedded in a tin-rich groundmass containing the antimony–tin δ solution. In the absence of antimony the copper–tin η solution forms with tin a eutectic containing only 1 per cent.

of copper; and the groundmass in Britannia metal may possibly be a eutectic of analogous composition.

Lead and Lead Alloys

The impurities present in soft lead, such as is commonly used for sheet, pipes, etc., rarely exceed 0·03 per cent. in total amount. The cast material usually has a large grain size (Fig. 331) and if cold-worked will recrystallise at atmospheric temperature. The metal is extremely weak, it may suffer deformation or creep under its own weight and is liable to intercrystalline failure under vibratory stresses on account of its very low fatigue limit. Very small additions of metals which were at one time regarded as undesirable impurities have a beneficial effect on lead for many purposes, on account of the increased strength which they impart to the metal. Thus, 0·5 per cent. of cadmium raises the fatigue limit to three times that of pure lead, and proportionately greater increases can be obtained by the use of ternary alloys containing about 98 per cent. of lead and consisting of lead, cadmium and tin or lead, cadmium and antimony. These elements form eutectics with lead, but the alloys used are generally within the limit of solid solubility at the eutectic temperature, and after casting in chill moulds, or quenching the reheated alloy, age-hardening effects of varying intensity are produced.

Antimony–Lead Alloys.—The solubility of antimony in lead decreases from 2·45 per cent. at 247° C. to 0·25 per cent. at 20° C. The solid solution of antimony in lead forms a eutectic with antimony (which contains some lead in solid solution) having an antimony content of 12·5 per cent. and a melting point of 247° C. The macrostructure of the 1 per cent. antimony–lead solid solution is shown in Fig. 329. The 2 per cent. antimony alloy as cast shows a structure of solid solution partly surrounded by eutectic (Fig. 318): it becomes homogeneous after annealing at 240° C. and quenching in water.

The 9 per cent. alloy consists of dendrites of the lead solid solution and eutectic in the ratio of about 1 : 2 (Fig. 319). Alloys containing from 5 to 12 per cent. of antimony are used for accumulator grids, and those with about 15 per cent. of antimony for bearing metals.

Calcium–Lead Alloys.—The alloy containing 3 per cent. of calcium has had a limited use as a bearing metal. It contains crystals of Pb_3Ca in a groundmass of solid solution of calcium in lead (Fig. 320). This solid solution may be obtained in the supersaturated condition by quenching, and the quenched alloys undergo age-hardening.

Bearing Metals

The anti-friction alloys, or alloys suitable for bearing metals, have a very distinctive appearance under the microscope. The essential property of an anti-friction metal is that it should consist of hard particles capable of resisting abrasion and bearing the load, embedded in a softer matrix which is capable of yielding slightly and adjusting itself to any local pressure. The most desirable character of the plastic matrix differs according to the load on the bearings and the working conditions. For example, for bearings which have to work under heavy loads, bronzes containing 10 to 15 per cent. of tin and phosphor–bronzes are frequently used. Such bronzes in the slowly cooled condition contain particles of the δ constituent (and in the case of phosphor–bronze particles of Cu_3P in addition) embedded in a matrix of the α solid solution (Fig. 281).

For bearings working under lighter loads, white metals are used. Typical white metals are the copper–antimony–tin alloys (Babbitt metals). Such an alloy used by the Navy contains from 2 to 7 (say $4\frac{1}{2}$) per cent. of copper, 8 to 9 per cent. of antimony, and the remainder tin. Tin containing upwards of 1 per cent. of copper shows needle-shaped crystallites of the copper–tin η solid solution (Fig. 321), a constituent formerly referred to as ϵ (p. 223). Alloys consisting

FIG. 326.—Transverse section of a rod of pure zinc, extruded at 340° C., showing allotriomorphic grains of the metal.
Etched in 5 per cent. nitric acid in alcohol.
× 500.

FIG. 327.—Transverse section of a rod of aluminium–zinc alloy containing 4 per cent. of aluminium, extruded at 340° C., showing zinc (α) and ($\alpha + \beta$) eutectic.
Etched in 5 per cent. nitric acid in alcohol.
× 500.

FIG. 328.—Transverse section of a rod of copper–zinc alloy containing 2 per cent. of copper, extruded at 340° C., showing grains of ϵ solid solution in a groundmass of η.
Etched in 5 per cent. nitric acid in alcohol.
× 500.

FIG. 329.—Macrostructure of an ingot of 1 per cent. antimony–lead alloy, $4\frac{3}{4}$ inches diameter and $15\frac{1}{2}$ inches long, cast at a temperature of 400° C. into a mould at 146° C. The pouring time was just under 3 minutes after which the ingot was fed for another 3 minutes. The fact that the stream of molten metal was not central, but nearer the right of this section, accounts for the displacement of the equiaxial region to the right, and the direction of the dendrites, tending to be upwards on the right and downwards on the left.
Etched with a solution of ammonium molybdate and citric acid. About half actual size.

PLATE LIX.

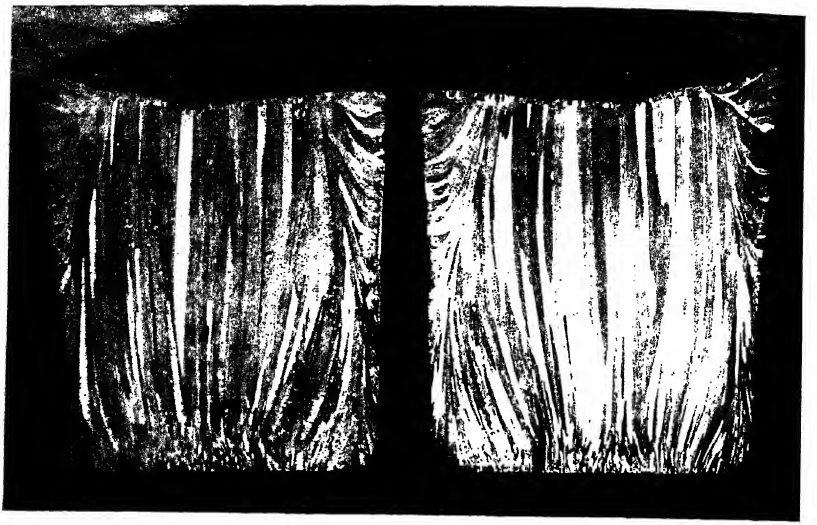
FIG. 326.

FIG. 327.

FIG. 328.

FIG. 329.

[*Facing p.* 262.



A FIG. 330. B

FIG.

FIG. 330.—Structure of an ingot of pure zinc cast by the Durville rotatory method into a mould of preheated refractory sides and a water-cooled copper base.

Two-thirds actual size.

The two halves of the ingot have been machined, A horizontally and B vertically as seen in the photograph. The cracks and tearing on A indicate the lack of strength and ductility of zinc across as compared with along the dendrites. The tensile strength along the dendrites was found to be about 4 times that across the dendrites. The hexagonal axis of the space lattice of zinc is transverse to the columnar crystals: the direction of growth is that of the basal plane of the hexagon.

L. Northcott: "The Effect of Cast Structure on the Rolling Properties of Zinc," *Journal of the Institute of Metals*, 1937, (1), vol. lx, p. 229.

FIG. 331.—Macro-structure of the axial section of a cast lead block, as used in the Trauzl lead-block test for explosives.

Etched in a solution of ammonium-molybdate and citric acid. Nearly half actual size.

Pure lead is cast in a steel mould 200 mm. diameter and 200 mm. high, the walls of the mould being 23 mm. thick and the base 30 mm. thick. The base carries a vertical core producing a central hole 25 mm. diameter and 125 mm. long. The casting is fed by a head 47 mm. wide and 100 mm. high, which has been removed from the block before it was photographed. In view of the possible variations in macrostructure, the specification rightly requires that blocks for comparative tests should be cast under identical conditions.

A. Marshall: "Explosives" (2nd edition), p. 469.

principally of tin but containing upwards of 9 per cent. of antimony, show hard cubic particles of the γ tin–antimony constituent embedded in a matrix of the δ solid solution of antimony in tin. The addition of copper reduces the antimony content at which the γ constituent appears and results in a hardening of the alloy due to the separation of a copper–tin constituent (the η solution) in the form of needles or star-like crystallites (Figs. 322, 323). These two constituents, the cubes containing antimony and the stars copper, are often referred to as SbSn and CuSn respectively, but they actually contain more tin than these compounds.

In some bearing metals the matrix consists principally of lead. Antimony–lead alloys show a eutectic at 12·5 per cent. of antimony. With more than this amount the alloy consists of hard crystallites of antimony in a plastic matrix of eutectic. The addition of tin as in Magnolia metal (lead 80, antimony 14, tin 6) further increases the hardness of these alloys, since the tin combines with some of the antimony giving the cubic crystals already described. Some tin passes into the eutectic in solution in antimony (Fig. 324).

The casting temperature and rate of cooling have an important effect on the size and distribution of the hard particles. If the alloy is cast in chill, the particles are small, but uniformly distributed: if it solidifies too slowly, they are large and tend to float to the top. Moulds are generally heated to about 100° C. and the alloy poured at a temperature just above the melting point.

The amount of the hardening elements, copper and antimony, which are added is limited by the fact that, when the hard particles of the alloy increase in quantity to such an extent as to come in actual contact instead of being merely embedded in the matrix, the alloy becomes brittle.

Practical Notes

Polishing.—The precautions adopted for very soft metals must usually be observed. Great care is necessary to avoid

the production of a flowed layer in tin and lead alloys during the preparation of the specimen. For cutting, a sharp well-lubricated hack-saw must be used. Any filing required must be done with a fine file and at a light pressure. Emery papers should be flooded with paraffin when necessary to reduce friction. After the specimen has been taken down to an old piece of 00 paper it will be ready for final polishing, which is best done by hand with liquid metal polish on selvyt stretched on a board. If the liquid is deficient in lubricating properties a few drops of paraffin may be added. The cloth should be kept very moist. The film of paraffin left on the surface may be removed by rubbing on selvyt moistened with benzene or acetone, or preferably by swabbing lightly with clean paraffin and washing first under a very strong jet of water, and then with acetone. The specimen is then given a very light polish by hand on selvyt with magnesia and water. Grinding and polishing must be sufficient to remove the flowed or recrystallised layer, and to aid in this the specimen may be etched and lightly repolished several times before the final etching.

Macro-examination of Lead Alloys.—Sections are prepared in the manner indicated above, with the object of producing a surface reasonably free from scratches and with as shallow a recrystallised surface layer as possible. This layer is removed by prolonged etching. Nitric acid in water, or nitric acid and ammonium molybdate in water may be used for preliminary etching. The surface should be swabbed continually with selvyt or cotton-wool, moistened with the solution, or pitting will result. If the alloy contains much antimony, an adherent layer presumably of an antimony oxide is formed and must be removed by rubbing. For this reason macrosections of antimony–lead alloys are not so readily prepared as those of other common alloys of lead. When the structure has begun to emerge, the surface may be finally etched with ammonium molybdate and citric acid which gives a much brighter appearance though its action is slow. The

surface should then be washed with water followed by acetone and allowed to dry in an inclined position (Figs. 329 and 331).

Etching.—The following reagents are suitable.

Zinc and Zinc Alloys

Hydrochloric acid: 1 per cent. solution of concentrated acid (sp. gr. 1·19) in alcohol.

Nitric acid: 1 per cent. solution of concentrated acid (sp. gr. 1·42) in alcohol.

Chromic acid: 6 grams chromic acid dissolved in 94 grams concentrated nitric acid and a few drops added to 50 c.c. of water (Timoféef's reagent).

Sodium hydroxide: 10 per cent. solution in water.

Tin and Tin Alloys

Hydrochloric acid: 5 per cent. in alcohol.

Acetic acid (as below) for alloys with lead.

Lead and Lead Alloys

Nitric acid: 5 per cent. in alcohol.

Acetic acid and hydrogen peroxide: glacial acetic acid to which is added hydrogen peroxide in amounts up to 3 per cent. The smaller the amount of hydrogen peroxide the less the attack on grain surfaces (revealing segregation, twinning, etc.) and the greater, relatively, the attack on the grain boundaries.

Acetic and nitric acids in glycerol: glycerol 4 parts, glacial acetic acid 1 part, concentrated nitric acid 1 part. The nitric acid is added immediately before use and the solution should be heated to a temperature of about 80° C. (Vilella and Beregekoff's reagent).

Bearing Metals (White Metals)

Nitric acid: 5 per cent. in alcohol for alloys rich in lead.

Hydrochloric acid: 5 per cent. in alcohol for alloys rich in tin.

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(References are to Figure numbers—not to pages.)

All except Figs. 50, 209 and 210 were taken by vertical illumination.

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